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CONTROL OF HAZARDOUS MATERIAL SPILLS

Environmental Protection Agency
Washington, D.C.

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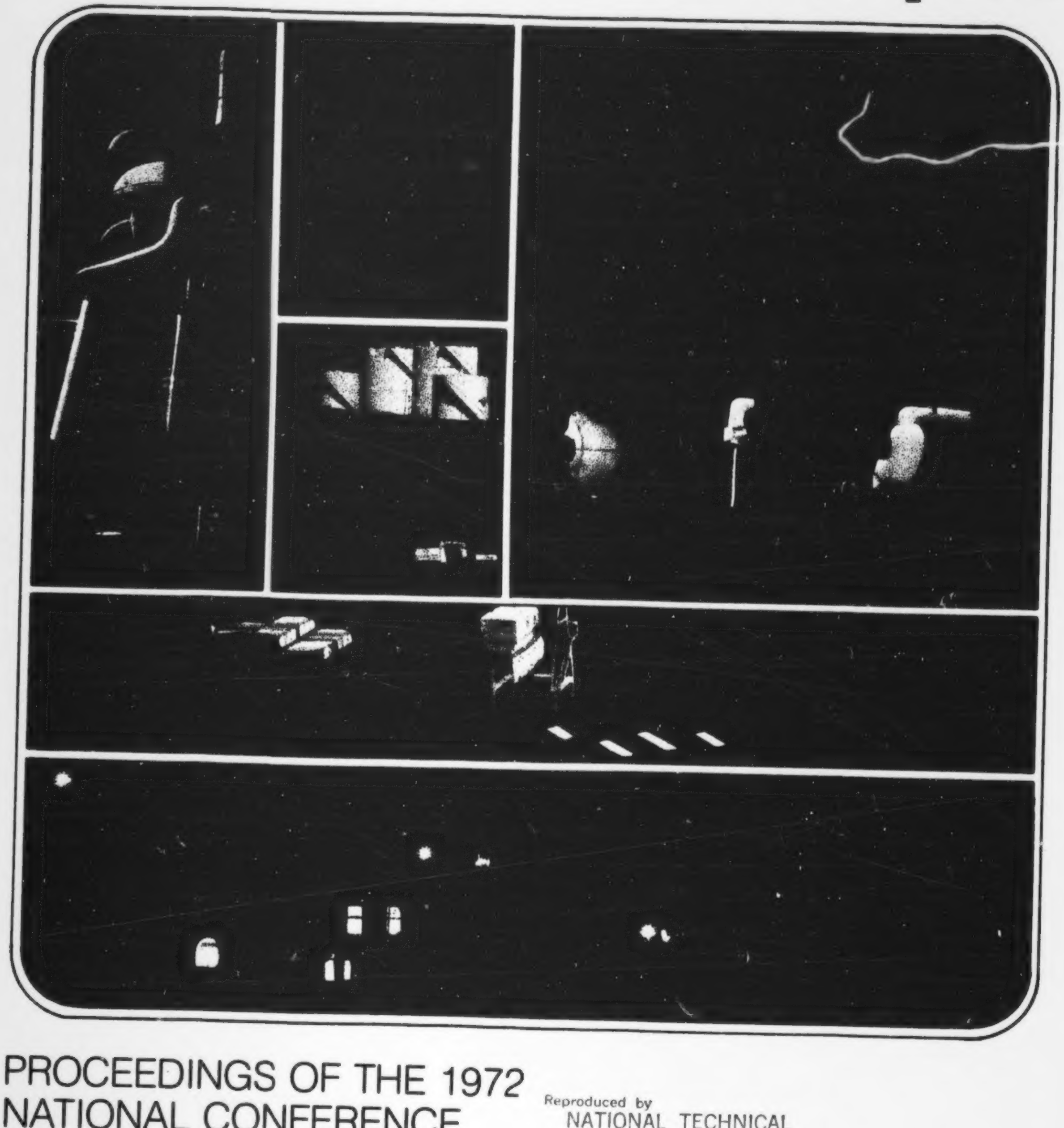

PROCEEDINGS OF THE 1972
NATIONAL CONFERENCE
ON CONTROL OF
HAZARDOUS MATERIAL SPILLS

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HAZARDOUS MATERIAL SPILLS — THE NATIONAL PROBLEM

LELAND D. ATTAWAY
Environmental Protection Agency

In a statement which I believe very succinctly describes the general feeling of the Nation, the President of the United States has said: "The nineteen seventies absolutely must be the years when America pays its debt to the past, by reclaiming the purity of its air, its waters, and our living environment. It is literally now or never".

The mandate leading to this statement comes in part from a long smouldering reaction by the people to the gross pollution which has been destroying the natural beauty and the quality of life in the United States, but it is also based upon hard scientific data. The biological sciences have provided alarms which quite rightly have given the solution of this problem such a high priority.

Through an increased understanding of the effects of industrialization, we have become very much aware that a natural balanced environment is a tightly integrated combination of chemical, physical and biological elements. A change of any one of these three may greatly affect the other two.

We know that a large number of trace elements and chemicals are quite valuable, in low concentrations, for maintaining the biological stability of a community. But although an organism may require the presence of these elements within a certain concentration range, in many cases an excess of these same elements can be toxic. For example, it is well known that zinc is an essential micro-nutrient. It has been found, however, that concentrations as low as 0.1 ppm will exhibit toxic effects on some fish.

In nature, the probability of gross changes of chemical properties, while present, is usually very small. These changes, as they occur, normally would be painstakingly slow compared to the rates of change we see today. The chances for excess concentrations to occur before the era of production of industrial chemical were very limited.

Now, through man's activities, this natural balance system has been subjected to an estimated 50 billion gallons per year of polluted water, 142 million tons of air pollutants, 360 million tons of garbage, and 1.5 billion pounds of industrial solid waste. The equilibrium between chemical, physical and biological elements has undergone a severe shift, very much to the detriment of the biological element. Quite rightly the President, Congress, and State Legislatures have spoken through increasingly meaningful legislation, and I'm sure it is clear to everyone that the waters, air and land are to be restored.

Estimates of the cost vary with the level of restoration, and the approach, but they range from $75-125 billion in the next five to ten years to obtain a quality of water environment essentially equivalent to 1915. As a percentage of GNP, however, which is one crude method for measuring economic impact, these costs are certainly well within the capacity of the nation. Annualized costs would run to 1.5% of the GNP.

It is the industrial revolution that produced this ecological imbalance. It now remains for an industrial resolution to correct it.

Added to this industrial resolution is a further need to prevent unnecessary spills or minimize accidental spills.

It is in terms of an environment far improved over the present situation that we must evaluate the impact of hazardous material spills. In view of the tremendous national effort and the important historical significance of this task, what would be the public reaction, to an industry which releases, over a period of one year, in concentrated slugs, at unexpected times and places:

1.7 Million # of sulfuric acid,
3.2 Million # of various industrial alcohols,
3.4 Million # of fertilizer solution,
44 Thousand # of phenol,
2-3 Million gallons of industrial wastes,
360,000 # of acetone,
600,000 # of various monomers,
3 Million # of other organic chemicals,
19,000 # of especially toxic materials, such as pesticides, or
2 Billion gallons of mining wastes.

These are undoubtedly only a fraction of the spills actually occurring, which include both in-plant and transportation spills. Many of these spills occurred in streams now biologically sterile from chronic pollution, and have escaped the widespread publicity which could occur. This will not be the case a few years hence.

Does the cost for prevention of spills compare to the environmental and human safety benefits recevied? Let's consider first the characteristics of a hazardous material spill—either through a transportation or in-plant accident.

The major characteristics are these:

First, not only are spills unpredictable as to time and location and type of waterway—but, in addition they vary widely as to the properties of the material. This makes response difficult—and requires a considerable amount of specific technical knowledge.

Second, spills often present immediate severe threats to human health, and in many cases the prevention of adverse environmental effects becomes secondary.

Thirdly, and this one is going to assume increasing importance, a spill may in a few hours cancel the results of years of environmental improvement efforts.

Fourth, from sad experience, we have found that very small spills of certain materials can have far-reaching effects.

So with these special properties of a hazardous material spill, it is apparent that we have the potential for undermining a large portion of our restoration effort from the aforementioned tremendous outlay of funds. A major improvement program is essential and now is the time to begin.

I would like to describe to you in very general terms first the legislative background relating to spills and then the effort that the Federal Government is making to provide its share of the solution.

Legislative Background

The Torrey Canyon incident in 1967 directed attention to the problem of immediate and long term damages to the environment from spills of oil. This, and subsequent major oil spills, resulted in correcting legislation as well as focusing attention on problems associated with accidents involving chemicals. The Water Quality Improvement Act of 1970, therefore, contained a specific section, entitled "Control of Hazardous Polluting Substances." This section required the promulgation of regulations designating hazardous materials.

It also gave the President the authority to establish means for the removal of such substances. Another provision of the section requires reporting of spills.

Also, when the owner or operator of a facility where a spill has occurred refuses to take appropriate action, the President is to have the authority to arrange for removal, at the owners expense.

The new clean water legislation under consideration by Congress, requires the Administrator of EPA to designate hazardous substances and to determine which of these hazardous materials are not subject to removal, once spilled into the waterway. EPA is then authorized to establish penalties (up to $14,000,000 for vessels) for the discharge of these materials into the waterways. When you consider that a large portion of the non-oil spills are not subject to removal from watercourses with existing technology, it becomes apparent that a very strong incentive for the prevention of spills is being introduced.

Under this legislation, EPA has directed an effort to the problem of hazardous material spill control. A national contingency plan has been established, and teams have been established at both headquarters and in the regions to meet this problem.

For general discussion, we have separated the problem of hazardous materials spill control into three lines of defense: 1. Prevention; 2. Countermeasures, and 3. Restoration.

Lets first discuss prevention, since the legislation to date has stressed this. I doubt if there are very many people closely associated with the problem who will disagree with this priority. The difficulties associated with protecting the environment once a spill has occurred are overwhelming in some cases—and prevention is perhaps the only method of attack.

An analysis of the limited number of spill incidents reported in 1971, shows that the spills are about evenly split between transportation accidents and in-plant occurrances.

The expertise for prevention of spills in processing plants certainly lies within the private sector. This technical expertise at this time is quite overwhelming and it certainly is not the desire of EPA to become deeply involved in the processing of chemicals. An extensive Federal System of plant inspections would not be in the interest of either the manufacturers, or the Federal Government.

The current legislative posture, leaning to heavy fines, allows each manufacturer or transporter to solve, in that way which is best for him, an industry problem which society will no longer accept. Each industry must maintain the integrity of the hazardous materials which are necessary in its line of business.

The usually excellent safety record of the chemical industry indicates that in-plant containment of the materials as it relates to human safety on plant property is under control. This protection must be extended to the environment, and to those outside the plant fence. The burden in this area certainly belongs squarely upon the management of the chemical companies.

Bearing in mind that the primary responsibility for prevention of in-plant spills rests with the manufacturer, EPA is willing to aid in the development of monitoring techniques, hold conferences such as this one, and to provide and exchange any technical information which might be requested. We can't and don't want to run your plants—but we do intend to monitor the results of your work—and insist that plant management also emphasize the environment.

The transportation industry, since it moves through public areas has traditionally been more closely regulated—once again toward this goal of prevention. The primary responsibility for the prevention of in-transit spills has been assigned by agreement to the Department of Transportation—with water transport falling under the Coast Guard. The point made earlier still holds—that although a good effort is now being made, further improvements are required to bring the spill level down to a value consistent with the effort being made to alleviate chronic pollution. Every cost benefit analysis considering the high cost of cleaning up oil spills has shown that prevention is the least expensive solution. This is equally true in the prevention and control of spills of hazardous materials.

Thus, prevention, the first and most important line of defense against spills, is the theme which runs throughout this conference.

Assuming that very great improvements can and will be made on the prevention of spills within the next few years we still must reluctantly face the probability that some spills will occur. Under the authority given by the Water Quality Act of 1970, EPA has undertaken research and development work aimed at giving the people who face the control of these spills in the field better tools.

The first need for applying countermeasures is an improved reporting and information system. Quick response to a spill is essential if any of the treatment systems are to have a chance of working. Keeping in mind the vast numbers of chemicals which can be spilled, a large amount of technical information must be available for the choosing of the proper countermeasure. Computerized information systems are being developed which will place this information in the hands of the people in the field.

For spills which are not reported, or for locating and following reported spills, there is a need for portable instruments which can be used for the detection and identification of an array of chemicals.

We are also making an effort to put together technology which will mitigate the effects of spills. The necessity for delivery on very short notice has introduced certain engineering constraints. There is little doubt that this second line of defense will be expensive to call in, and we must remember it will mitigate, not eliminate the damage to the environment. Keeping in mind the variety of properties which one can expect to face, it is apparent that there will not be one cure-all countermeasure for all spills.

The development of countermeasures is an area where the private sector has apparently had no economic incentive to enter, and one where a large void exists.

Restoration, returning of the damaged environment to its pre-spill condition, can be a sad and expensive task faced by the spiller. The effects of a shock exposure to extremely high concentrations has an effect which can be different than the same material slowly metered into the environment, and we have some very expert presentations on restoration in this conference. In this act, we survey the failure of our prevention program and our countermeasures program and try to rebuild to the natural environment. In most cases this requires the disposal of any remaining pollutants and setting the stage for nature to cure its wounds. Restoration is an aspect that can be minimized by an aggressive prevention plan.

Since a spill, when it does occur, must be handled under crisis conditions, it is extremely important that the procedure for handling of spills be previously thought out and that cooperation between the state agencies, industry, and the Federal Government be obtained. Because of the many overlapping areas of responsibility this is no small task.

The Federal Government, through an inter-agency agreement has attempted to put its own house in order. Under this agreement DOT has prime responsibility for the prevention of accidents while in transit. EPA has the lead responsibility for prevention of in-plant spills. Once a spill threatens a watercourse, EPA has lead responsibility. Thus, the EPA lead in the counter-measure programs.

As a further effort to provide pre-planning for the handling of spills, the Council for Environmental

Quality has, as directed by the Water Quality Act of 1970, established a National Oil and Hazardous Substances Contingency Plan. This plan establishes an organization for handling spills which are beyond the capability of regional teams.

The cooperation between industry, the states and the Federal Government has been rapidly improving as everyone realizes the importance of attacking this problem. There is no doubt that the increased effort to prevent and mitigate the effects of spills will intensify the need for still closer cooperation.

To summarize, a significant reduction in the amount of hazardous materials being spilled into the environment is required to conform to the National Effort for A Restored Environment. Prevention should be the main thrust. It must be the industrial sector which applies its technical and managerial expertise to lead the way.

Efforts for the second line of defense, containment and treatment, will be dictated by the success of the prevention program, and hopefully will get smaller.

Restoration will be required, I'm certain, but it too should become minimal and insignificant with time, depending upon the degree of success of the other two more important aspects.

We at EPA and I'm certain this is true of our other participating agencies, are anxious to have industry take the leadership in these areas, and to have the Federal Government participate and cooperate with you to help you resolve your spill problems.

A STATE'S APPROACH TO THE PROTECTION OF THE ENVIRONMENT FROM HAZARDOUS MATERIAL SPILLS

JAMES B. COULTER
Maryland Department of Natural Resources

INTRODUCTION

There are fifty states, the District of Columbia, and several territories. Thus, there are many approaches to the problem created by the threat of hazardous spills reaching the waters under their jusrisdiction. These differences are justified by the variation in circumstances that create the problems.

While most of the elements of the problem are common to all of the jurisdictions, the significance of any one element will vary from State to State based on such things as the location, density, and types of activities posing a hazard. The nature of the water system, the health and environmental implications of a spill, the travel time between the site of a spill and sensitive areas, the amount of hazardous material that might be released, and the toxicity of the substances released are some of the factors to consider. There are many others including transportation, storage, and handling of any particular substance of concern. Another set of variables is created by the behavior of the substance upon spilling, the severity and persistence of resulting damage, detection and analytical confirmation of spills, and the potential for concentration and magnification in various life forms.

In the discussion that follows, the specifics will pertain to one state, Maryland, but this state might serve as a good case study. Maryland has been described as "America in Miniature," and the description certainly applies to the waters of the state. Surface waters include mountain trout streams, major rivers, estuaries varying in size from the largest to the smallest, and the waters of the Atlantic Ocean itself. The same might be said for the ground waters; however, with the time allotted for this discussion, emphasis will be placed on the state's approach to the control of spills of hazardous substances into surface waters.

There is another factor that makes Maryland an attractive case study. Water pollution control at the state level is a long established and vigorous program. The threat of hazardous spills is recognized in the form of state legislation and regulations which have the force and effect of law. The state agencies have accumulated a significant background of experience in dealing with spills ranging from the ever present small discharges of oil to oil spills measuring in the thousands of gallons. While oil is perhaps the most common experience, there have been emergencies created by spills of a variety of other toxic substances.

Spills are Inevitable

Even though prevention is by far the best practice, control agencies base their plans and programs on the assumption that spills of hazardous substances are inevitable. The situation is quite similar to the familiar problem of fire prevention and fire fighting. While a community strives to prevent fires, the prudent community maintains an effective fire fighting organization.

The program in Maryland is based on the assumption that spills will occur and that the time and location of a spill is an activity correlated statistical event. There are hot spots where spills are likely to occur. These include storage and transfer points and industries where hazardous materials are processed and stored. There is also correlation with internal changes in commercial activities. Experience has shown that when processes are started and stopped, spills of an intentional or accidental nature are more prone to occur.

The time and location of spills during the transportation of hazardous materials is more indeterminate. These events include accidents such as the collision of ships and the derailment of railroad tank cars. They also include the accidental rupture of pipelines. Another random hazard is created by major storms. Storms increase the hazard of transportation and may interrupt power supply thereby causing spills from emergency by-passes at pump stations or at critical points in industrial processes. Possibilities that we do not like to contemplate, but nevertheless exist, include disruptions during war time or the effects of deliberate sabotage.

Prevention

In Maryland, prevention is the first line of defense. To be most effective, experience has shown that prevention must be a requirement of law in addition to being a matter of cooperation and good citizenship. The laws are strong in this regard. The discharge of any toxic substance is a violation and the responsible party is subject to civil or criminal prosecution depending on the circumstances.

It is unlawful to construct an installation or conduct an activity that might result in pollution of the state waters without first receiving a permit from the water pollution control agency. Before issuing a permit, the pollution control agency is required to evaluate the activity and cause preventative measures to be constructed and maintained. In that regard, the law specifically stipulates that the control agency may require plans, specifications and other information that it deems necessary to see that antipollution safeguards are provided.

To control spills, the state routinely requires such measures as back-up power systems, terminal ponds at the end of emergency overflow pipes, impoundments or other containment areas around critical storage and processing sites, and the installation of alarm systems to signal accidental spills.

A typical example is a newly installed oil transmission line. The pipeline conveys oil from a dockside terminal at Piney Point, Md. to a power plant located 32 miles away at Morgantown on the Potomac River. Control agencies preferred that oil for the power plant be transmitted by pipeline rather than by barge. This insistence was based on the observed reduction of oil spills and accidents incurred by pipeline transmission as opposed to those that occurred during the transportation, loading, and unloading of oil barges.

Even though the possibility of an oil spill was reduced by utilizing pipeline transmission, the state insisted on elaborate safeguards where the pipeline crossed the Wicomico River. In addition to the obvious safeguards to prevent mechanical accidents to the pipe, the pipe itself was the subject of special design. Oil is transmitted through an inner pipe wrapped with a layer of insulation. The insulation is jacketed and the insulated pipe is layed within a larger diameter pipe with a void space between the two. Both the inner and outer pipelines are designed to take a stress far greater than that exerted by the oil before rupture will occur. The void space between the pipes is filled with an inert gas and the pressure of the gas is monitored. Any leakage of the inner pipe will cause an immediate change of gas pressure which will be signalled and transmitted to the control recorder. The recorder actuates a device which stops the flow of oil until the trouble is located and conditions are returned to normal.

To implement water pollution control laws, regulations are adopted. A specific regulation covers the transfer and storage of oil and other hazardous substances. As part of the regulation, the state requires that employees who are active in the transfer of hazardous materials be instructed in safe procedures both verbally and in writing and that they be reinstructed in proper procedures on a periodic basis. Furthermore, a person who is trained in preventive and emergency measures and who is a designated representative of the company must be in the immediate vicinity of the operation during the entire time when a hazardous material is being transferred. When warranted, these procedures are included as a requirement of the company's permit and the permit may be rescinded if the condition is violated.

Enforcement and Liability

Laws are more effective when liability for violation is fixed in a quick and meaningful procedure. In Maryland, liability is attached to accidental as well as deliberate spills of hazardous materials.

Violations of water pollution control laws are punishable as either a criminal or civil offense depending on the circumstances. A conviction could result in a fine of $10,000 or a year in jail or both, and the activity causing the pollution can be enjoined. Maryland's Attorney General prosecutes water pollution offenders and Special Assistant Attorney Generals are assigned on a permanent basis for that purpose.

A powerful provision of Maryland law provides that the responsible party must pay for damages to the environment. Several recent examples illustrate the application of this law to several types of spills.

In the western part of Maryland, a state owned trout hatchery is located on a stream that provides the very high quality water needed. The Texas Eastern Transmission Corporation operates a gas well field upstream from the hatchery. Wastes are contained in a lagoon.

In 1966, the lagoon sprung a leak discharging a highly turbid drilling mud waste into the creek. The leak was discovered in time to remove trout from the hatchery before a kill occurred. Damages were assessed against the company and the company paid $1,638.99 for costs incurred in moving the fish out of the hatchery and returning them when the danger was past.

No further trouble occurred until August of 1969. At that time, wells were being regenerated with a hydrochloric acid solution. Acid escaped from the lagoon and as a result, 28,000 hatchery trout were killed.

In this instance, replacement of the resource in kind was more important to the state than their monetary value. The Attorney General brought action and required the company to replace the fish with trout of the size that they would have obtained at the time of replacement had they not been killed. The company delivered to the hatchery 35,000 trout with an aggregate weight of 11,667 pounds. In addition, the company paid $1,469.82 for clean up of the hatchery after the fish kill.

Another type of kill occurred last fall. The Bethlehem Steel Company was forced to make preparations to close down because of impending labor trouble. During that period, citizens observed and reported a fish kill in Bear Creek which adjoins the plant property. The state made an investigation and concluded that Bethlehem was responsible for the death of 177,500 menhaden and 50 striped bass.

The state charged Bethlehem Steel with the cost of the fish that were killed and requested payment. Bethlehem denied responsibility for the fish kill but paid $16,000, the amount charged by the state.

In July of 1970, an oil spill occurred in Baltimore Harbor. A barge operated by the Harbor Towing Company was taking on oil from the Humble Oil and Refining Company pier. Pumping continued after the barge was full and approximately 68,000 gallons of oil spilled into the harbor. It was reported that the operator was found asleep in his cabin aboard the barge at the time the oil spill was discovered. Criminal charges were brought against the towing company, the oil company and the employee. The towing firm pleaded "No Contest" and was fined $7,500. The oil spillage charges are pending against Humble Oil and Refining Company and the employee.

A pipeline rupture was involved in an oil spill in September of 1970. Oil was found leaking into a branch of the Gunpowder River. In excess of 7,000 fish were killed. Investigation showed that the oil was leaking from a pipeline and the owner, Colonial Pipeline Corporation, was billed for the fish kill. The company paid $2,098.62, representing the full amount billed to it.

Maryland's law is such that the money recovered from fines levied for damage to the environment is deposited to a special fund. Money from the fund is used to repair damage to the environment to the extent possible. While on the surface the fines might appear small, their collection and the public attention focussed on the cases thereby, are proving to be an effective deterrent to loose practices that result in spills of hazardous material.

A special section of Maryland law deals with vessels discharging oil. Except during periods of emergency, it is unlawful to discharge oil, and any person who discharges oil or observes an oil discharge is required to report the incident to the State Department of Water Resources. Failure to report a discharge of oil carries the same penalty as other violations of the water pollution control law—up to $10,000 fine or one year imprisonment or both.

Clearance from ports of vessels guilty of discharging oil may be withheld until all liability for the oil spill is satisfied. The penalty for a spill constitutes a lien against the ship. Included in the liability are the costs incurred by the Maryland Port Administration and other agencies of the state for labor, materials, and other costs incurred in cleaning up and restoring the damaged areas.

Tankers entering Maryland to unload or receive oil cargo must post a bond of at least $100 per gross ton of oil cargo. Should oil be spilled, the bond can be forfeited to the extent of liabilities for environmental damages and clean up costs. The bond is not released until the control agency certifies that the vessel has not been a source of oil spillage. The owner of any vessel which is not bonded and enters Maryland to discharge or take on oil is liable to a find of $5,000; excep, if an owner demonstrates adequate evidence of financial responsibility to the federal government, it is exempted from Maryland's bonding requirement.

Response to Spill Emergencies

Word of spills of dangerous materials reaches the state from several sources. Water quality monitoring equipment is another source of information. All field personnel of the Department of Natural Resources including game wardens, marine police and fishery biologists as well as water pollution control workers report any evidence of a spill to a central alert location. State police report highway accidents where a spill of hazardous materials have occurred to the water pollution control agency. Frequently, the state is alerted to a spill by private citizens who have observed a fish kill, an unusual color, or oil.

When a report is received, it is immediately relayed to the radio room of the Fish and Wildlife Administration. In accordance with a standard operating procedure, the report is relayed to the duty officer of the state's water pollution control agency. Depending on the time of day, the duty officer uses his office or home as the spill communications center and takes charge of the situation until he is relieved by his superior. When the duty officer is notified of a spill report, he follows a prearranged procedure. He either goes to the site or dispatches other natural resource personnel near the site to verify the situation and obtain the crucial initial information.

The duty officer identifies downstream water users, including sources of municipal water supply, and calculates the time that it will take for water to flow from the site of the spill to water intakes. Information is relayed to health officials and critical water users as rapidly as it is received.

The duty officer may use any personnel or resources of the Department of Natural Resources to obtain crucial information as quickly as possible. This includes the exact location, the nature and the extent of the reported disturbance. Suspected sources of a possible spill are identified and investigations are initiated as quickly as possible. The priorities of the duty officer are: first, protect public health, natural resources and property. Second, identify if possible the source of pollution and bring it to a prompt halt. Third, initiate clean up and other counter measures. Fourth, initiate the investigations that will lead to prosecution and assessment of liabilities.

After the initial report and investigation, resources of the state are brought to bear as necessary. Where damage to aquatic life has been observed or where there is reason to believe that it has occurred, biologists go to the scene and conduct investigations including the collection of samples of living and dead fish and other organisms. The first notes made by the biologist on the scene are often the most revealing.

Samples of the spill material and water are obtained and dispatched to the laboratory for chemical analysis. In the laboratory, fish and other aquatic life samples are examined by biologists for symptoms of disease, injury, or of toxic substances.

As early as possible, a project manager is appointed and he relieves the duty officer. The project manager is responsible for correlating the information from all of the various sources, for evaluating the information being obtained to insure that it will be complete, and for the preparation of a spill report essential to the legal action that will follow.

In these situations, it is highly desirable for the state to maintain a close working relationship with federal, interstate and local agencies that may have concurrent responsibilities. After the first priority steps are taken to prevent health hazards and minimize environmental damage, the U.S. Coast Guard, the Environmental Protection Agency, and other federal agencies are alerted. The same is true for agencies of local government and for interstate commissions that might be involved.

Maryland, West Virginia, Virginia, and the District of Columbia are members of the Interstate Commission for the Potomac River Basin. When a spill occurs in the Potomac, the commission headquarters serves as the communications center. A plan for emergencies created by spills of hazardous materials has been developed by the Commission. This plan provides for the necessary interstate exchange of information. It also provides for the protection of health, natural resources, and other aspects covered by Maryland's plan.

In Baltimore Harbor, the possibility of a hazardous spill is great enough to warrant investment in standby equipment and supplies. Whenever a spill is discovered within the Harbor, the Maryland Port Administration is responsible for prompt containment and clean up. To accomplish this mission, the Administration has equipped itself with oil recovery vessels and a tug with four scows for holding material recovered from the water. A crane truck is utilized to lift scows loaded with the recovered material from the water for transport overland to final disposal sites. The Port Administration is also equipped with 3,000 feet of 6 inch diameter boom and two types of expendable absorbents to contain and clean up oil spills.

Pending Legislation

Maryland's General Assembly is now in session and it has under consideration several bills which will strengthen the state's program to cope with spills of hazardous substances into its waterways. One of the bills provides for licensing of all shore based oil terminals. Tanker terminals would be licensed by the State Department of Natural Resources and the license fee would range from $250 to $25,000 per year based upon the size and capacity of the facility. A license would be denied if the terminal was not provided with appropriate anti-pollution safeguards.

Money received by the Department of Natural Resources would be deposited into an Oil Disaster Research Development and Contingency Fund. The fund would be permitted to build to a maximum of $2,000,000. When it reaches that amount, the license fees would be adjusted downward to maintain the $2,000,000 ceiling. Money from the fund would be used to clean up oil spills, to buy equipment for that purpose and to conduct research and development aimed at reducing the damage created by oil spills.

A second piece of legislation of great interest extends the state's authority to collect for damages done to the environment as a result of pollution. The present law, as previously discussed, allows recovery of damages to the environmental resources of the state. The law pending before the General Assembly would extend this principle to private property damaged by pollution and would require the state to collect for damages to private as well as public property.

SUMMARY

Maryland has a vigorous water pollution control program typical of that in many states. Maryland's protection of the environment from hazardous materials spilling into water, while unique to the circumstances of the state, covers elements of the problem common to all of the States.

Prevention is the first line of defense, but the program is based on the safe assumption that spills will occur even with the best preventive measures in effect. Thus, provision is made to protect health and environment, contain and clean up spills, identify and prosecute violators, and fix and collect damages.

THE MANAGEMENT OF HAZARDOUS MATERIALS IN THE ENVIRONMENT — A VIEW BY INDUSTRY

RUSSELL C. LUDWIG and JULIUS E. JOHNSON
Dow Chemical Company

Commitment to the best practical moral as well as legal responsibility is the cornerstone for management and stewardship of hazardous materials. This principle is applicable to every person and to groups of persons involved in any phase of handling of such materials.

We can learn a good deal from experience in similar situations of management and stewardship and apply tested concepts to the subject of this conference.

It is interesting to note some statistics on personnel safety in industry over the past twenty years, as shown on Figure 1. We know that personnel safety depends on good design, and is synonymous with the safe operation and handling of equipment and material.

More attention to mechanical improvements achieved a significant step in the forties. As we learned from the leader in industrial safety achievement and found by experience, the tougher part of improvement in personnel safety is the human element. This demands commitment, involvement, communication and motivation of each and every person in the operation from the president to the janitor and back again. Commitment sets the work environment and this must be supported by training, attention to detail and continual evaluation to assure that we adhere to the best practices and that we really practice what we preach.

Preplanning, preparedness and effective communication networks are essential elements for safe operations and prevention of and/or appropriate action in case of hazardous materials spills.

We have followed chemical plant environment in correlation with toxicological work since the thirties as a preventative measure because of our desire to protect employees and the public when our chemicals are involved.

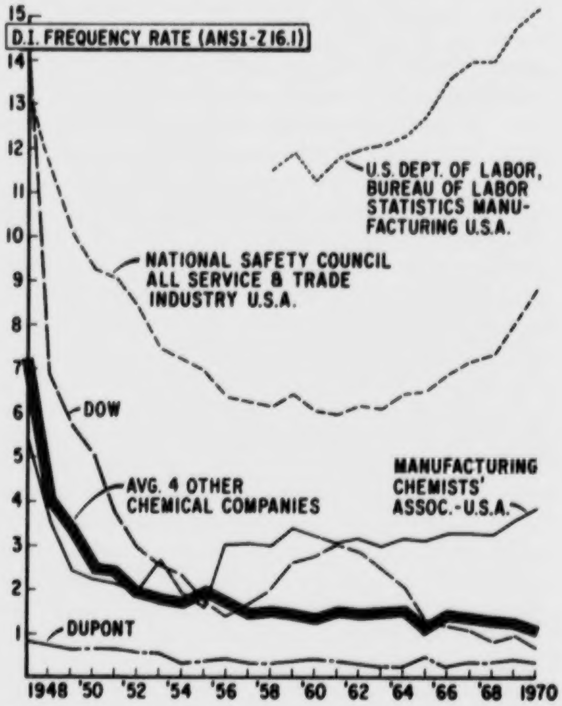

Figure 1: Comparison of Disabling Injury Frequency Rates—National Statistics Vs Chemical Industry and Six Largest Chemical Companies

Dow has been active in the National Agricultural Chemicals Association (NACA) and its emergency system for responding to spills of these materials. For many years we have had a nationwide Dow system for responding to any transportation spill of our materials. This was formalized into a uniform system

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in 1969. Recently Chemtrec has developed a similar industry-wide system that we are using in parallel to our own.

Physical properties and toxicological data of hazardous material must be *pre-determined* to prevent problems and to have information readily available to assist in prompt and proper response to accidental spills. Advance information to and collaboration with carriers and protective agencies, such as fire, police and health authorities, are essential to appropriate first response to any hazardous exposure. As in our safety programs, dry runs and simulated emergencies must be used to test and audit the communications and response systems—*again* continual attention to detail.

Several of our own experiences on spills will illustrate these points. Our Midland, Michigan, plant is located on a small stream, the Tittabawassee, which becomes a trickle in the dry season. Technological improvements are aimed at reduction of wastes at the source. Treatment ponds, protective dikes, around the clock monitoring of plant waste water, closed loop cooling towers, emergency diversion and holding ponds and total recycle closed loop plants have been improved and added to continuously since the thirties. A year ago we spent over a million dollars to add a safety diversion system with leak detectors, and alarms with safety valves to guard against possible plant spills getting to the river. One plant scheduled to be shut down within a year was protected with all of the detecting devices, and depended on shut down in case of a leak, and was not tied into the diversion system.

A malfunction in a level control allowed a few hundred pounds of caustic to go out the barometric condenser. The detection system worked, the red lights and alarms worked, but a human element entered at this point. An operator became unsure of which valve to close and spent several critical minutes finding a supervisor. The safety valve was closed and the plant shut off. But some of the caustic did get to the river. I repeat, there is a real need for continual training and dry run experience to keep any system viable.

The *unexpected* incident causes the accident, and again in hazardous material spills as in personnel safety, the auditing of systems and plans and alertness to new possibilities is the continual challenge.

Another incident involving a train derailment at Port Hope, Ontario, bears out the need for predetermination of properties of material and effective communications systems.

A dozen cars derailed and jumbled down a thirty-foot embankment with wheat, empty bourbon barrels and a 4,000 gallon tank of Dow weed killer that was under the pile and leaking at an unknown rate. At this point, containment and handling of the clean-up would have been a problem, but not an emergency. However, Murphy's law added another of its unexpected happenings to the equation and introduced the emergency factor. A severed fire hydrant added an estimated 250,000 gallons of water in the half hour before it could be shut off, and this flushed a large amount of wheat and the initial spill of chemical over the concrete seawall and into the boat harbor 100 feet away. The city of Port Hope had its drinking water intake one-half mile down the lake. The emergency communications system worked and paid off. Railroad men called the Dow emergency number on the bill of lading and critical information was given over the phone for proper action at the wreck area, including the shut off of the Port Hope water intake. This was followed up by technical men to the scene.

Toxicity, solubility and flammability data were used. Analytical methods were available to assure that no chemical had reached the drinking water intake area. Most of the chemical was recovered from the leaking tank car, but biodegradability data also were needed to insure proper disposal of the wheat, chemical, debris and soil at the site. The information was quickly put to use. No human exposure or environmental damage resulted. The emergency system and the people involved functioned smoothly.

Hazardous materials spill prevention is our goal, as prevention is our prime goal in the area of personnel injuries and fires. We must concurrently develop and improve our ability to cope with the unwanted accident to minimize the effects.

Design is an important aspect, and this must be continually improved through development and application of technology.

Detailed investigations of 60 major spills in the chemical industry have shown that over 60 percent are due to human error. We find five basic causes of these poor operations that resulted in accidents and spills: poor supervision; inadequate operator training; failure to use prescribed procedures and precautions; mishandled or misunderstood communications; and individual attention to detail and accountability.

From our own experience in prevention and handling of personnel injuries, fires and spills at The Dow Chemical Company and the shared experiences with many others, we have proven the need and value of the concept of total commitment and follow up action.

I would like to touch on regulations for a moment. Good management will usually be ahead of regulations, and laws and good regulations, many times, are a result of best industry practices. Regulations are necessary to set attainable goals, to give uniform understanding and performance measurements, to challenge and discipline in a positive way, to set priorities and urgencies. Capricious or vindictive proposals may make headlines, but hinder real progress.

Referring again to Chart I, I feel that the upswing in industrial personnel injuries called for regulations that resulted in the Occupational Safety and Health Act (OSHA). If everyone had DuPont's record, regulatory priorities would have been elsewhere.

This conference and its noted speakers and subjects will cover in detail the many aspects and scope of the problems of hazardous material spills.

We feel so strongly about the need for moral commitment and stewardship by industry that we will risk redundancy and summarize these keys to implementation:

- Total involvement of a company from top management through every level and function within the manufacturing process itself and in conjunction with carriers and terminals and advice and support to the customers.
- Candid and supportive communications with local, state and federal agencies and legislative bodies.
- Pre-determination of human safety and environmental hazards that may be caused by our materials—both to prevent problems and to control them if accidents occur.

We need to emphasize prevention, but also to plan for the unexpected. This involves the development, testing and maintenance of emergency procedures and communication networks within plants, with carriers and with public emergency personnel and regulatory bodies.

PROCESS PLANT DESIGN FOR CONTROL OF HAZARDOUS MATERIAL SPILLS

J. W. CORLEY
Celanese Chemical Company

The Celanese Chemical Company Clear Lake Plant began operations in 1967 with facilities for producing acetaldehyde. Since then the plant has been expanded to include facilities for producing acetic acid, vinyl acetate, ethylene oxide, ethylene glycol, diethylene glycol, triethylene glycol, and methanol, with a total capacity of well over two billion pounds per year. During planning of the original plant it was agreed that environmental concern would be a major factor in dictating design criteria. This paper specifically presents the Clear Lake Plant design for control of hazardous material spills.

The prime means for control of any spill is a proper drainage system. At the Clear Lake Plant we designed an integrated system that we call "multimoat" fail-safe drainage. The first part of this multimoat system was designed so that any liquid (either from a chemical spill or rainwater) drains into the plant rather than out of the plant. Since the land is naturally quite flat, extensive work was required to establish elevations satisfactory for effective drainage. A ditch system was installed to transport any liquids to holding ponds. Figure 1 depicts this rainwater ditch drainage system. Any liquid in the ditch system may be trapped by closing sluice gates or diverted to either of three ponds—BOD holding pond No. 1, BOD holding pond No. 2, or to the "clean" retention pond No. 3.

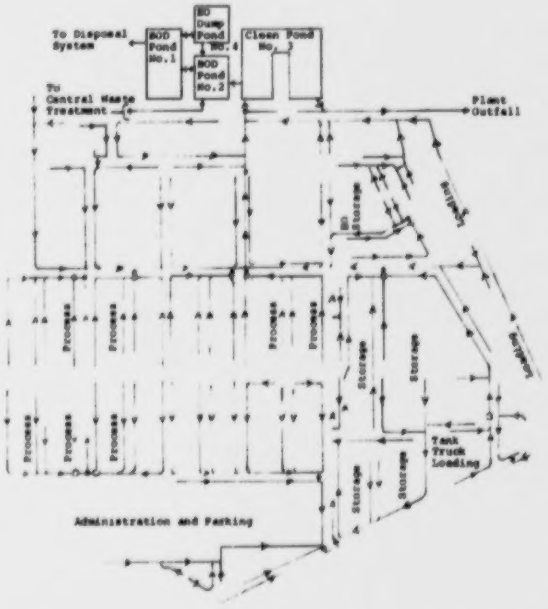

Figure 1: Rainwater Ditch Drainage System

During normal operating conditions the ditches are opened into the clean retention pond. When flowing, the drainage ditches are routinely sampled every four hours and analyzed for chemical contamination. If contamination is found, the water flow is diverted to one of the BOD holding ponds, depending on the amount of organic contamination present. The contents of pond No. 1 are sent to a deep well disposal injection system.

Pond No. 2 is normally pumped to a central waste treatment plant, but may be pumped to Pond No. 1. The clean pond, No. 3, is allowed to drain off the plant property and even though the water entering the clean pond is analyzed, additional samples of the pond itself are checked prior to allowing any flow to leave the plant site. If it is found to be contaminated, the clean pond may be pumped to pond No. 2, but neither pond 1 or 2 may be pumped to the clean pond No. 3. By having complete control of the drain-

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age system we are assured that only uncontaminated rainwater leaves the plant property.

The multi-moat concept of isolation and drainage control was followed in designing the layout for each of the process units. Equipment with high spill or leak potential was identified, such as transfer pumps. Also, specially designed sampling systems, including closed collection lines and holding sumps for sample flushings, etc., were identified as high spill potential. This equipment was placed inside all other equipment at ground level and an "inside drainage flume" installed. (For precious liquid spills, such as liquid catalyst solutions, curbing around the high potential spill area may be used if desired. This material could be drained into a special holding sump for recovery.) The process unit concrete foundation floor was poured with the proper grade to insure drainage into the inside flume. During normal operations this flume is continuously flushed with a small volume of water. Liquids from seal flushings, pump leaks, sample spills, etc., are washed into collection sump No. 1 (see Figure 2). This material is then pumped into the process effluent system for treatment. There is no choice as to where this material is pumped—it always goes into the process effluent system, which is a closed system of pipes and storage tanks that tie into our disposal system.

All process units have roofs that cover the high-risk areas. On these roofs are located some of the smaller-risk items with flanged joints; for example, heat exchangers. Drainage from the roof area, usually only during rainfall, is diverted through down spouts into an "outside flume". The objective here is to minimize process area which receives rainfall as part of the overall objective to minimize the volume of waste treated. This rainwater flows through the outside flume into the rainwater drainage ditch and into collection sump No. 2 (see Figure 2). Note: During periods of slight rainfall the outside flume is diverted to sump No. 1 and treated in the same manner as material from the inside flume. If there is sufficient rainfall to flush the outside flume clean, as determined by laboratory analyses, then the flow is diverted to sump No. 2. This material may then be pumped through BOD pond No. 1 to the disposal system, or if completely free of contamination, diverted through the ditch drainage system into the clean retention pond No. 3. This concept of isolation and drainage control permits segregation of process effluent from each process unit. After segregation has been achieved, a decision can be made as to where the material is to be pumped for treatment.

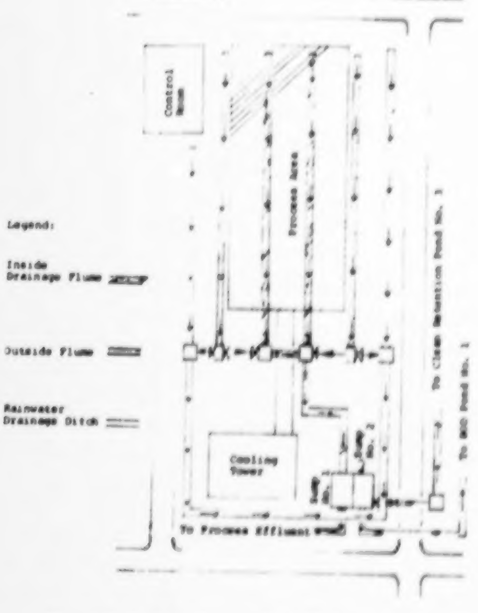

Figure 2: Typical Process Unit Drainage Plan

It was no real problem to design and install this multi-moat fail-safe drainage system—it just required money. Of course, it's helpful to have creative people who are interested in making the system work. As an example, we ran into a problem when we put the system into practice. A common fault with sluice gates or ditch valves is they always seem to leak, or seep—at least the ones we purchased did. To correct this we have installed fail-safe valves which we call the Walling valve. It's called the Walling valve because it was invented by Mr. Harold Walling. He works in our plant engineering group. The valve is simple, but does not leak or seep. If anyone is interested in the valve design, contact us in about six months—after we have checked the patent rights.

If there is a particularly hazardous materials unit, this same concept may be used for complete isolation. For instance, at the Clear Lake Plant we consider ethylene oxide (EO) to be particularly hazardous. Figure 3 shows a special dump line running from that part of the process containing high concentrations of EO, from the EO tank car washing/loading rack, and from the EO storage tanks to the EO Dump Pond No. 4. If for any reason high concentrations of EO must be dumped, it will be diluted with a large volume of water in the EO Dump Pond. This will quench and control any exothermic reaction. The contents of the Dump Pond may then be pumped through Pond No. 2 to the central waste treatment plant, or through Pond No. 1 to the disposal system. Note: Although not shown on Figure 4, the EO unit contains the same type ditch drainage system—inside drainage flume, outside flume and two collection sumps as the other process units discussed earlier.

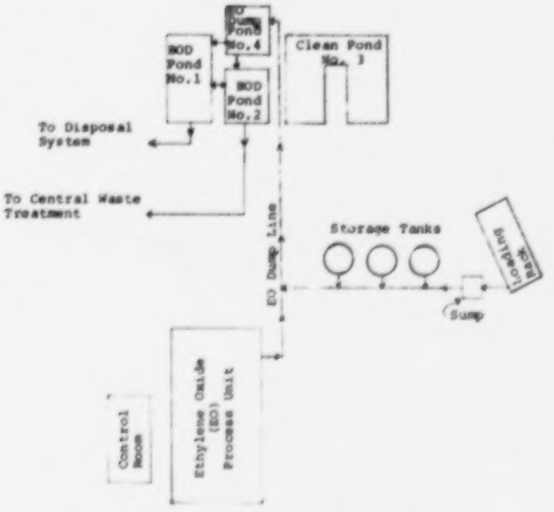

Figure 3: Ethylene Oxide Emergency Dump Line

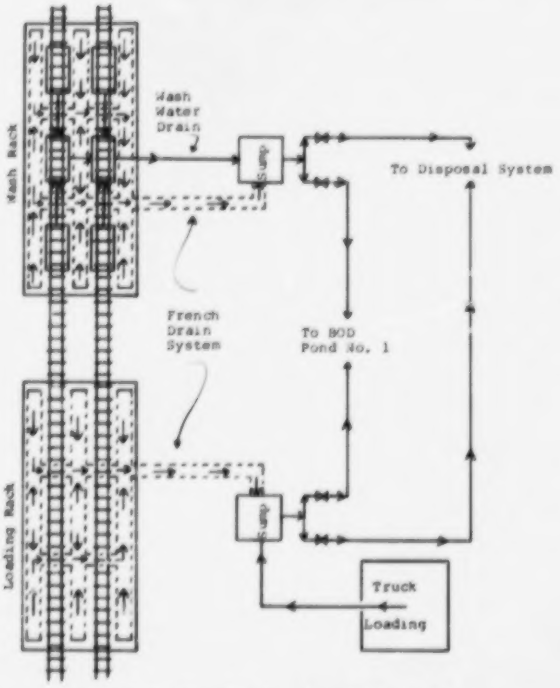

Figure 4: Washing/Loading Area Drainage System

Again, this same concept was used to design the tank car wash rack, the tank car loading rack and the tank truck loading area (see Figure 4). Each "spot" on the wash rack has a grated, open drainage sump below ground which drains into a collection sump. In addition, French drains were installed on each side of the railroad track, and gravity feed into the same collection sump. The contents of this sump may be pumped directly to the disposal system or through BOD pond No. 1 to the disposal system.

French drains were also installed on each side of the track at the loading rack, but drain into a separate collection sump. This sump may also be pumped directly to the disposal system or through BOD pond No. 1 to the disposal system. The tank truck loading area drains through a closed pipe into the same collection sump used by the tank car loading rack. All grades and elevations were constructed to assure satisfactory gravity drainage to the collection sumps.

One last word on controlling spills. The Clear Lake Plant also has barge loading facilities available for use. We have a two pipeline system to the loading dock. Where our pipelines emerge from the ground, we installed a sunken, curbed concrete ramp (see Figure 5). This area slopes to the center so that any liquid will flow through grated area into submerged holding tanks. We also have specially designed loading arms with a drain cock at the bottom elbow bend to allow complete liquid drainage back into the holding tanks after loading is complete. Drip pans are used under all flanged connections during loading and these are emptied into the holding tanks. The contents of the holding tanks may then be pumped into a truck for transporting back to the plant for reclaiming. Even though we are discussing liquid spills rather than vapor and odor control, we have installed an interesting vapor collection system at the barge facility. A giant "vacuum cleaner" is hooked onto the barge vapor ports, sucking the loading vapors into a collection header. sufficient excess air is allowed in the collection header to stay below the explosive range, and this mixture is burned in a smokeless incinerator to control odors and vapor emissions during barge loading operations.

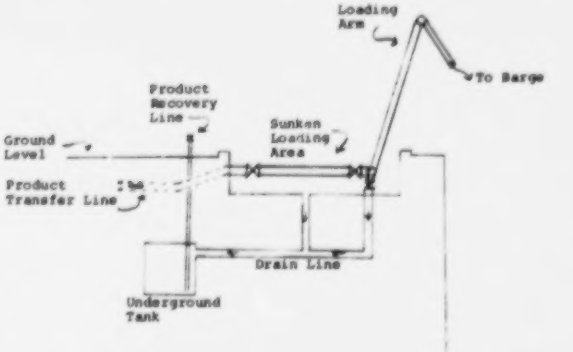

Figure 5: Schematic of Barge Loading Facility

But then vapor control is a separate topic altogether—isn't it?

CONTROL SYSTEMS FOR PREVENTION OF HAZARDOUS MATERIAL SPILLS IN PROCESS PLANTS

JAMES L. KERN
Monsanto Company

This paper deals with the design of control systems to prevent hazardous material spills. It has been the author's experience that most spills in the process industry are caused by operator error or, unfortunately, by the failure of a control system. The intent of this paper is to describe how controls can be applied to prevent or at least warn of an impending spill.

In common useage, the words instrumentation and control are sometimes used interchangeably. Since the attendees at this conference are from many fields, I would like to define the terms.

> Instrumentation is the art or science of applying measuring devices, or measuring and controlling devices to an object or combination of objects (a system) for the purpose of determining the identity and/or magnitude of certain varying physical or chemical quantities, and often for the purpose of controlling those quantities within specified limitations.

The object or combination of objects (system) to which instrumentation can be applied in the process industries include a specific apparatus such as distillation column, an evaporator or a reactor; or an entire processing system, such as a continuous spinning line in a textiles plant or a catalytic cracking unit in a petroleum refinery. Of course, there are hundreds of such applications in this area.

The physical or chemical quantities which are the objects of measurement and which are often subjected to automatic control are termed variables and are many in number. These variables include temperature, pressure, flow, specific gravity, speed, viscosity, consistency and chemical composition—to name just a few. The application of digital computers in the optimization and supervisory control of processing units and the oft referred to term, "automation", also come under the general heading of instrumentation and control.

Controls are installed in process plants for specific purposes. One of the more important is to maintain a high level of product quality; that is, to regulate the operations in the process within the parameters which will result in the most efficient operation of a given unit or plant. A process control system operates on the basis of detecting the difference between the value of the variable being controlled and the value desired. Once this difference or error is detected, the controller initiates corrective action to return the controlled variable to the desired set point by manipulation of the process through a final control element such as a control valve. Automatic control can perform this function much more efficiently than human operators, particularly where high speed response is necessary. Other functions of instrumentation and control are minimizing operating costs by reducing the number of people required to operate a plant and maintaining the yield of a plant at a maximum level through adherance to precise operating conditions. The latter reduces the quantity of unuseable by-products or wastes requiring expensive disposal.

In summary, a control system makes use of sensing devices to measure the condition of a variable, compares this measurement with a setpoint, which has been predetermined, and initiates action through manipulation of the process or energy stream to restore the variable to its setpoint. It is important that we understand that instrumentation and control systems cannot work beyond their capabilities. For

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example, in most installations, the final control element is a control valve that is dependent upon a pressure drop equivalent to roughly one-third the total system pressure drop in a pumping system for proper operation.

If the pump's efficiency decreases or the line begins to plug, the pressure drop available across the control valve decreases and further opening of the valve will no longer maintain the correct flow. Once this happens, the system is no longer under control, and the flow will continue to fall off despite the control system's efforts to restore it to proper operation.

The concept of applying instrumentation and control to prevent the spill of a hazardous material or any material, for that matter, is really nothing new. We have seen that instrumentation normally maintains smooth and efficient operation of a chemical process by keeping the operation within pre-determined specifications, and that it has a vital role during abnormal situations to trigger corrective action or, in extreme cases, to safely shutdown the operation or plant.

We know that something abnormal has to occur before a situation will develop that can result in a spill. As mentioned before, an operator can make an error and accidently overflow a vessel, a control system can fail whereby a runaway reaction occurs resulting in emergency venting of its contents or rupture of the reactor, or a vessel or pipeline can fail mechanically during normal operation causing the release of hazardous materials into the operation area. Frequently, the real test of the design engineer's skill results not from the design of the control system to handle the plant operation during normal situations but to design a control system that will handle an operation during abnormal situations.

The literature is abundant with references on the dynamics of process control and unit operations; however, this area is understood by relatively few. A thorough analysis of even a relatively simple operation often requires the use of sophisticated computer programs and a thorough understanding of the total plant system. To design for every eventuality, is, of course, expensive. The proper application of controls can reduce this expense. There are, of course, extreme situations where the plant must be overdesigned to handle every eventuality. But let's see how we can effectively use instrumentation and control to prevent the spill from occurring in the first place.

In so far as hazardous material spills are concerned, the control system should perform the following functions:

1. Determine that something is wrong.
2. Initiate corrective action to return the operation to normal.
3. Signal operating personnel that an abnormal situation has occurred.
4. In the event that the operation does go out of control, provide safe disposal of the overflowing materials in accordance with a pre-determined plan.
5. Signal that relief or overflow systems are being used.
6. If required, determine the nature of the released materials.

Only the first three items listed above are concerned with preventing a spill; however, we must consider the possibility that corrective actions will not be effective, and a means must be taken to handle the situation when the spill has occurred.

Let's examine each of these functions individually.

1. **Determine that Something is Wrong**

When dealing with a hazardous operation, it is normal to use redundant instrumentation, particularly for sensing the process variable. If temperature is a critical variable, then a separate temperature measuring device will be installed along side the primary temperature measuring element. In some cases, it is desirable to use a device having a different principal of measurement as a backup. This would be the case where a thermocouple is being used as a sensor for normal temperature control of a reactor. The backup device could be a resistance bulb located in the reactor near the thermocouple. The resistance bulb would be connected to a different instrument on the panel board in the control room.

In an instrumentation system, the measuring element is the least reliable part of the system because it is exposed to the usually extreme ambient conditions of heat and corrosive vapors or gases. There have been situations where we have utilized as many as three different sensing devices whereby the operator was signaled if there was a pre-determined deviation in reading between any two of the measurements.

Safety monitoring systems can be used to indicate the existance of an abnormal operating condition, or they can be designed into a more sophisticated system that determines the rate of change of the operation away from its normal condition to indicate the severity of the upset. These techniques can be used on all normal measurements of flow, temperature, level and pressure.

The use of analyzers to monitor process vapor or gas streams is also quite common and can be applied to warn of an abnormal change in composition of the process stream which could result in the rupture of the pipeline or processing vessel.

There are now safety devices available which detect the beginning of an explosion in a vessel which are designed not only to detect the existance of this condition but also to release a suppressant which prevents the explosion from occurring; the entire sequence takes place in a few milliseconds before the internal heat and pressure builds up to a dangerous condition.

2. **Initiating Corrective Action**
The corrective action to be taken when a hazardous situation is known to exist depends entirely upon the nature of the hazard and the consequences to the plant or operation. Sometimes the corrective action is taken in steps. In the case of the runaway reaction, the activation of an emergency cooling system may restore control without damage to the process material. If this action fails, and the temperatures and pressures continue to rise, materials that are designed to stop the reaction are admitted into the vessel. If this fails, then the materials are often released to another vessel which is specifically designed to handle the runaway batch. Such precautions are usually taken where there are several reactions in a given area.

An emergency control system almost always contains an electrical interlock system that shuts down pumps and closes values to prevent the flow of additional materials into the vessel that is out of control.

3. **Signal Operating Personnel**
There are several ways to advise operating personnel that an operational abnormality has occurred. The most commonly used method is to provide an alarm device in the instrumentation sensing lines. The switch is usually set to operate at some pre-determined level just above normal operation to draw the operator's attention to the particular control loop. This switch activates an annunciator consisting of a flashing light and a horn, which can be silenced upon acknowledgement by the operator. The flashing light ceases and is replaced by a steady light that illuminates a back-lighted nameplate indicating the operating unit where the abnormality has occurred. Operation of the alarm switch should be independent of any control mechanism so that the alarm will still function properly even though a malfunction might occur in the control mechanism.

In the case of extreme situations, the alarm device should be activated by the backup sensor previously discussed.

Activation of this alarm indicates that a hazardous situation exists and should sound an audible alarm different than the alarm system that indicates a minor deviation from control point. This is usually a louder horn or a siren which might also signal a condition requiring evacuation of personnel from the operating area. Alarm systems can also be obtained which incorporate the use of pre-recorded messages on tapes to indicate the nature of the problem for the operator.

4. **Provide Safe Disposal of Venting or Overflowing Materials**
The technique used in disposing of spilled or vented material, whether it is hazardous or not, is primarily a process problem. It is obvious, however, that the designer must consider carefully the requirements of instrumentation in a disposal system to assure its proper operation when called upon.

When gaseous materials or vapors require venting it is usually done by means of an automatic pressure relief system consisting of a pressure relief valve and/or a rupture disc. The vented materials are then released into a collection system or vented to the atmosphere directly or through a flare system. Selection of an automatic pressure relief valve must be done carefully. The valve must be sized to pass the quantity of material that has been determined by considering all the sources of the vapor or gas, and its temperature, specific gravity and relief pressure.

The selection of the rupture disc system requires knowledge of the same parameters with special emphasis being placed on the temperature to which the rupture disc is exposed. As you know, the strength of a metallic rupture disc is dependent upon its operating temperature, and rupture discs are designed to blow out at the specific pressure and temperature.

In a closed system handling liquids, the use of a pressure relief valve is also used to vent excess liquid under pressure which might occur from over filling a vessel or from external heat sources.

In the case of a runaway reactor requiring the dumping of the vessel's contents, the dump valve must be triggered by some sort of a control system that senses the condition requiring dumping. The sensor, as mentioned before, is usually one of the backup measuring devices that activates a control system, which consists of electrical logic that opens the valve. The valve can be driven by either an electrical motor or by a pneumatic or hydraulic piston to assure positive action. Limit switches are generally used on this type of valve to indicate that the valve is closed for normal operation and that it has opened in the event of an emergency situation.

It is common practice for a routine maintenance procedure to be developed for each of these types of relief devices to assure that they will be in operating condition when called upon. These procedures consist of actual operation during simulated over pressure situations as in the case of relief valves, or by periodic operation manually in the case of the bottom dump valve.

Excess flow valves are in-line safety devices that act to limit the flow of liquids or gases out of a pressurized system. They will pass normal rates of flow; however, they will close against excess outward flow rates in the event the pressurized system is opened to the atmosphere due to pipe breakage or because of system misoperation. These devices are used extensively in pressurized liquified petroleum gases and in chlorine tank car discharge lines.

5. **Signal that Relief or Overflow Systems are being Used**

This has been partially covered earlier by the use of limit switches on valves or by alarm signals from the secondary sensors. Operation of a relief valve is generally indicated by the installation of a pressure gauge on the downstream side of a relief valve. This pressure device can be used to signal that the valve is open as a result of an over-pressure. There are cases, where the vapor is extremely hazardous, that the rupture disc is installed downstream from a relief valve to contain any materials that might collect due to a slow leak in the relief valve. In such cases, the pressure gauge technique also indicates that the relief valve is leaking.

When liquid materials are vented or dumped, a flow switch or a level probe can be installed in the normally empty pipeline to indicate that liquid is flowing by that route.

6. **Determine the Nature of the Released Materials**

Some type of analyzer is usually the only acceptable means of determining the nature of the vented or otherwise released material. Gas analyzers can be used which are located in the operating area to detect the release of hazardous materials, or analyzers suited for the purpose can be installed in pipelines or vessels receiving the spill to indicate its composition. Since analyzers are normally a complex device requiring routine maintenance, their use is usually limited.

The application of instrumentation and control for the prevention of hazardous material spills must be made with great care. The sensing portion of instruments are, by their nature, a mechanical device. Measurement of flow, level and pressure is for the most part essentially that of measuring a pressure or pressure drop which requires the movement of a bourdon tube or diaphragm. This movement is sensed by a lever system, which also has the means of adjusting the calibration of the device. The movement of the level system is detected by either an electronic or pneumatic amplifier and converted into a useable electronic or pneumatic signal which is transmitted to the instrumentation in the control room. The process piping to the sensors must be designed to remain open and clear despite conditions that might tend to cause build-up of material or plugging of the sensing lines. Sensors must also be installed so that they can be isolated from the process for routine testing.

The use of thermocouples, resistance bulbs, strain gauge pressure transducers and capacitance level probes are, of course, electronic in nature and do not require a mechanical linkage system. While the use of thermocouples in capacitance level probes is quite common for detecting abnormal conditions, the use of strain gauge type pressure transducers requires expensive electronic equipment and careful calibration restricting their use for most processing applications.

The use of safety instrumentation must be carefully justified because it is easy to increase the cost of the plant to the point where it is no longer economical. It is far better to minimize the use of complex instrumentation through better process design techniques. Instrumentation is not a panacea, and controls are just one part of a complicated system made up of pumps, pipes, reactors, heat exchangers, and other processing equipment. Many operating problems are blamed falsely on faulty instrumentation when the real problem has been caused by a pump that failed or pluggage of a section of process piping.

Control panel displays must be designed with the operator in mind. It is important that he not only monitor the instrumentation before him, but learn to interpret the information that the instrumentation is providing for him so that he can correctly determine that an abnormal situation is developing, diagnose the cause and take corrective action before it is too late.

In summary then, apply instrumentation and control to keep your plant running smoothly in accordance with the objectives you have set for the operation. Use separate instrument and control systems to detect abnormally hazardous situations and to initiate corrective action. Make it easy for the operator to diagnose his problem, and keep the control system as simple and as easily maintainable as possible.

OPERATIONAL AND MANAGEMENT CONSIDERATIONS FOR THE PREVENTION OF HAZARDOUS MATERIAL SPILLS IN PROCESS PLANTS

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Proper plant design and the provision of effective control systems are necessary to minimize spill potential in a process industry such as petrochemicals manufacture. The full utilization of these facilities and further associated efforts in plant operation are essential for an effective prevention program. The following discussion is primarily directed at those contributions to spill prevention that require initiation or continuing supervision by operating facility personnel.

From a practical standpoint the phrase, "prevention of hazardous material spills," would be more correctly stated as "efforts to minimize the loss of materials which due to their properties, quantity and duration of loss, or characteristics of the receiving water, pose some hazard." A zero spill frequency is an impractical goal for industry considering present technology. The trend in industry for larger facilities and higher individual productivity, however, results in a greater potential for material spills in hazardous quantities and calls for increasingly effective programs of prevention to even keep pace with the growing potential.

The items discussed in the following paragraphs do not represent an exhaustive list of methods to improve spill prevention. They are largely drawn from personal experience and observation.

The essential management contribution to a successful program of spill prevention is that of commitment. Design features and control systems intended to minimize spills are of little benefit unless backed by a commitment for their proper utilization. The existence of this commitment is adequately demonstrated by the many design features and control systems in use today that have resulted from requests and efforts of persons directly involved in plant operations.

Since facility design and control systems for spill prevention are the topics of two associated papers, they will not be further discussed here except as they apply to other considerations and efforts applicable to spill prevention that are initiated by those responsible for the operating facility.

Assignment of responsibility to the smallest supervisory unit size practicable is generally recognized as an effective management approach to improve performance. This is applicable to the area of spill prevention. Generally the supervisory unit would correspond to the smallest group of facilities that are physically separable from others in terms of measurement of pollution loadings. The performance of the unit is more meaningful if spills are contrasted against the normal pollution discharge from the supervisory unit rather than only as isolated information. This, of course, requires adequate measuring equipment to allow loads to be identified to the responsible source. Either actual experience or the association of a high loss-potential with a supervisory unit may further dictate the use of continuous monitors to better reduce the extent and duration of spills.

Source department responsibility for prevention of spills includes consideration of improvements in development of annual performance objectives. Likewise, the department should investigate the circumstances surrounding all significant, but less

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than hazardous, spills, provide effective means to avoid a repetition, and be alert to the applicability of such corrective actions to any other similar potential sources within the supervisory jurisdiction. The occurrence of a spill of likely hazardous consequences should further lead to a formal investigation of the type conducted following a major process failure or a serious personnel injury.

Proper communications concerning spills and their prevention should be a prime management objective. This requires the fostering of an atmosphere which promotes frank and open exchanges, and this is difficult because of the human desire to wish to conceal mistakes, even though it is largely from mistakes that we learn how to improve. The development and use of sophisticated monitors has done much to eliminate any concealment of losses. Open communication of management goals related to spill prevention can be an effective means of improving employee commitment if such goals are actually being pursued and are not just meaningless declarations. Communications that alert proper personnel in the plant to new facility startups, changes in process chemicals, new operating conditions, or any other unusual step, can be a very helpful aid in rapid spill source identification. Communications with sister operating plants, other companies, and regulatory agencies, relative to losses or new prevention techniques can accelerate overall program improvements and may avoid multiple occurrences of the same type of spill in different facilities.

Management and process supervision need to review existing operating practices and procedures for the purpose of making revisions to minimize spill potential. These considerations should also include maintenance practices and system shutdowns for repairs. In many cases the penalty to the operation is slight compared to the added protection. New facility design or revisions and alterations to existing manufacturing systems should be reviewed for adequacy of spill protection by operating personnel experienced in pollution control. This can be a prescribed step in project approval procedures.

Any discussion of management efforts relative to spill prevention should also include actions needed following the inevitable spill that will occur. Although it is too late to prevent the spill, nevertheless, there are actions that can prevent unwarranted concern or reactions on the part of others downstream, and can also prevent loss of time for those who need to respond. The principal actions needed are to rapidly recognize that a spill is occurring, to minimize the total loss to the receiving water, and to determine the spill quantity and duration. Another important action is the use of a spill evaluation procedure to provide a rapid assessment of probable consequences to the receiving water and its uses. A further action is to promptly and properly communicate spill and evaluation information to those who should know of it. These actions require effective monitoring systems, prior accumulation of pollutional properties of materials that might be spilled, and basic data concerning characteristics of the receiving stream. Analytical methods that are applicable in the concentration ranges needed should be available so that the path of the spill and its assimilation may be readily traced and prior estimates of concentration confirmed.

Those items that have been discussed for prevention of material spillage into receiving waters are just as applicable and important to abnormal losses of materials into sewers leading to wastewater treatment facilities. This is because a material loss may upset the treatment system, producing a poor quality effluent which may cause an undesired impact on the receiving water, much the same that would result from a direct spill.

Since spills or abnormal losses are almost always of useful products or intermediates, there is considerable economic justification to provide facilities and procedures to prevent such occurrences, apart from the fines and adverse publicity that can be avoided.

One tool (seemingly not available) that needs to be developed to aid management efforts to prevent spills is a broadly applicable performance standard against which progress can be measured and realistic goals set. By analogy to the field of personnel safety, where such standards are reported to be of significant benefit, a spill performance standard should compare both frequency and severity of spills against some measure of total risk, such as pounds processed, or pounds processed times processing steps. Those charged with overall program responsibility for personnel safety at a plant location can, through the use of frequency and severity statistics, relate their accomplishments and goals to the entire industry. This builds desired objectivity into program assessment. A comparable means of measurement would be equally useful for spill prevention programs.

The purpose of this paper will have been accomplished if it serves to stimulate and bring forth additional concepts that will better equip the process industries to deal with this significant problem area.

THE SPILL PREVENTION, CONTAINMENT AND COUNTERMEASURE (SPCC) PLAN OF THE REFUSE ACT PERMIT PROGRAM

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One of the charges to the United States Environmental Protection Agency (EPA) is to protect the Nation's environmental resources, such as our waters. The beneficial uses of water, which are (1) public water supply, (2) fish and wildlife habitat, (3) agricultural use, (4) industrial use, and (5) esthetics and recreational use, may be severely stressed by hazardous materials spilled into our waters. This paper focuses on what can be done to prevent these unplanned probabilistic discharges.

A hazardous material is proposed to be defined as one which is detrimental to these beneficial uses, by being any of the following:

a) a biologically accumulative poison,
b) lethal to aquatic life,
c) stress-causing, because of its severe biochemical degradability, or corrosivity,
d) growth inhibitory or stimulatory,
e) radioactive.

Biologically accumulative poisons are those substances not necessary for the survival or reproduction of the life form, and not detoxified or degraded within the organism, which are concentrated during ingestion, absorption, or adsorption by the organism to the point of toxicity to the organism, or to its predator in the food web. Since this definition implies some degree of persistence, the effects of the poison may be chronic, not necessarily acute. But the end result may be toxicity to some species because of the biological magnification throughout many life cycles if the material is especially persistent, such as polychlorinated biphenyls (PCB's).[1]

Substances lethal to aquatic life can cause extensive damage, especially if released as a slug in a slowly moving stream. Recently a spill of only 2,000 gallons of ethylbenzene wiped out all fish in the first 3 1/2 miles and caused additional damage even further downstream. In all, more than 13,000 fish were killed, and one public water supply intake was shut down until the material had passed.

This spill from an industrial facility occurred when material under high temperature and pressure was pumped to a diked holding tank. Apparently, the material flashed as it entered the tank, blowing the manhole off, and spraying material over and beyond the dike itself.[2]

Substances which are biochemically oxidized to form materials which again enter the food web present a unique situation if there is a major spill. This happens because the natural biochemical oxidizing mechanisms at work oxidizing the spilled material which is present in excess will consume all the dissolved oxygen (DO) present, and oxygen replenishment by natural aeration or photosynthesis is a slow process. Recently, a retaining wall broke, releasing over one hundred thousand gallons of chicken manure suspension. This material, traveling as a slug seven miles long, killed over one million fish which died literally of suffocation.[3] The manure presented such a biochemical oxygen demand (BOD) that all dissolved oxygen was consumed, leaving none for the fish or other oxygen-consuming life forms. In addition, the lack of dissolved oxygen causes an anerobic condition which in itself can interfere with some beneficial uses of water, such as water supplies, esthetics and recreation.

Growth inhibitory or stimulatory chemicals (such as phosphate fertilizers) promote the growth of some biological species to the point of creating an imbalance in the ecosystem. Although this problem is associated primarily with the continuous discharge problem, the ecosystem imbalance occurs largely because of the total amount of material involved. Thus, a spill of these substances adds further to the imbalance, and should be avoided.

Recently a waste storage pond broke, releasing 2 billion gallons of waste material from phosphate mining operations. The material ran more than 50 miles down a river and turned the receiving bay "into a giant vanilla milkshake."[4] The point to be emphasized here is not the fish kill which took place in the river, but the longer range imbalance caused by this large amount of phosphate.

Finally, radioactive materials are considered hazardous because of their potential damage to human health and latent danger to the environment. Although the discharge of such substances is regulated by the Atomic Energy Commission (AEC), their regulations can permit a sudden release of radioactive materials in a short period of time. EPA does have the responsibility to the public to protect its health and welfare from any materials which pose such an imminent and substantial danger.

These examples, plus literally scores of such incidents every day, illustrate that our aquatic environment is subjected constantly to needless stress, stress which may be significantly mitigated by preventing spill incidents. The primary interest of EPA is to prevent environmental damage. Industry will recognize this approach since prevention of spills of raw materials and products mean prevention of economic loss.

Working with the U.S. Army Corps of Engineers, the efforts of EPA within the past year to control pollution to our waterways by the application of the River and Harbor Act of 1899 (Refuse Act) have received widespread attention. This act makes it unlawful (with some exceptions, such as municipal treatment systems or ships) to discharge into the navigable waters or their tributaries without a permit. The application for this permit is formally handled and processed through the Corps of Engineers, with EPA having authority and responsibility for the evaluation of the pollutional aspects of such a discharge, and for informing the Corps as to whether or not the permit should be issued on this basis. The basic relationships between the applicant, the appropriate State regulatory agencies, the Corps, and EPA are depicted in Figure 1.

Since the Permit Program must be flexible to address the diverse problems of different industries in different geographical areas, this flexibility is achieved by attaching a variety of Special Conditions to the basic permit. One of these Special Conditions is the requirement for a Spill Prevention,

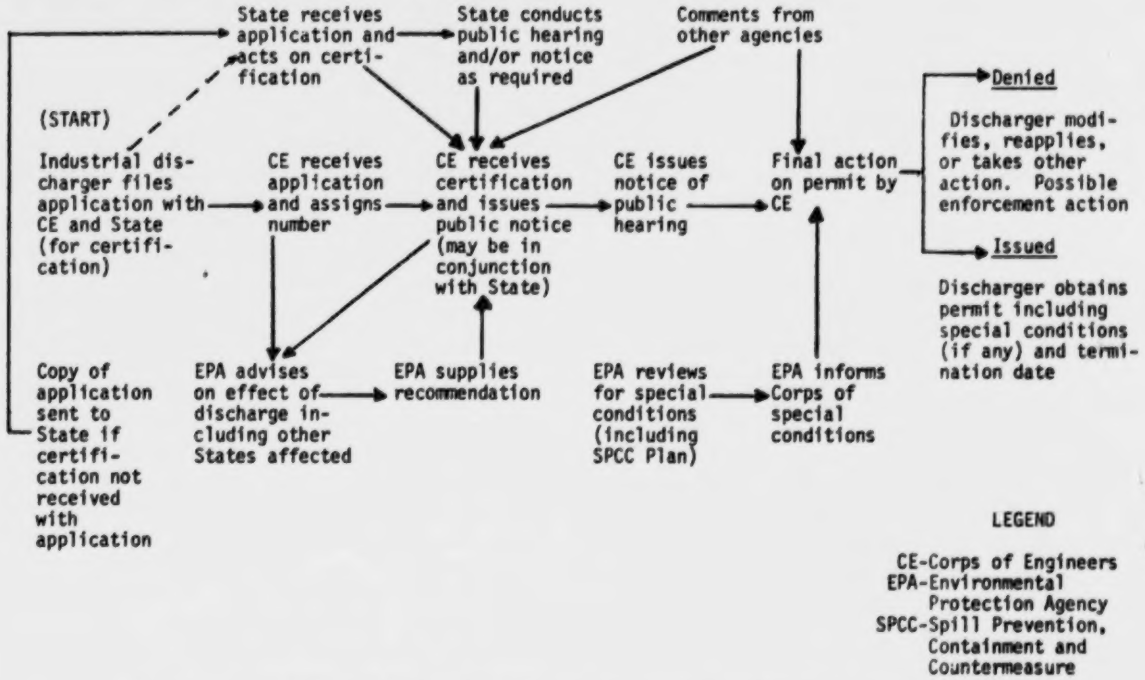
State receives application and acts on certification
State conducts public hearing and/or notice as required
Comments from other agencies
(START)
Industrial discharger files application with CE and State (for certification)
CE receives application and assigns number
CE receives certification and issues public notice (may be in conjunction with State)
CE issues notice of public hearing
Final action on permit by CE
Denied
Discharger modifies, reapplies, or takes other action. Possible enforcement action
Issued
Discharger obtains permit including special conditions (if any) and termination date
Copy of application sent to State if certification not received with application
EPA advises on effect of discharge including other States affected
EPA supplies recommendation
EPA reviews for special conditions (including SPCC Plan)
EPA informs Corps of special conditions
LEGEND
CE-Corps of Engineers
EPA-Environmental Protection Agency
SPCC-Spill Prevention, Containment and Countermeasure

Figure 1: General Flow of Permit Application Procedures, and the Prevention Plan Special Condition

Containment and Countermeasure (SPCC) Plan. The objective of this Plan is to document the fact that the facility has taken reasonable precautions to prevent and to contain and apply effective countermeasures to spills and to notify appropriate authorities.

The Permit Program then, gives EPA a means to address pollution at the source. It gives breadth to our overall program which includes such other activities as monitoring and enforcement. By using the permit itself to limit pollutants from a continuous (or planned) discharge, and the SPCC Plan Special Condition to address the problem of the spill (or unplanned) discharge, we place the responsibility of controlling hazardous materials on those most familiar with their physical and chemical properties and processing characteristics.

From the preceding discussion, it should be obvious that many industrial processing facilities now have many elements of the Plan, even though these elements have not been thought of or documented from an anti-pollution viewpoint. A dike around a tank farm of flammable materials is a fairly universal requirement for an adequate insurance program. In addition, it can prevent spilled material from reaching our waterways if designed with this additional requirement in mind. A training program for processors which emphasizes personnel safety and housekeeping may also emphasize collection of spilled materials for reprocessing.

In short, the development of an effective SPCC Plan starts with a great deal of background and relevance to current processing techniques; but, in addition, it requires a reassessment of the entire facility and its methods of operation from a new viewpoint: prevention of pollution from spills of hazardous polluting substances.

The Guidelines (Annex A) are meant as guidelines or suggestions to illustrate current EPA thinking on the problem of pollution prevention. They are based on sound engineering and operating practices drawn from the experiences of many of our leading processing firms. Consequently, they should receive careful attention and thought. While it is believed that adherence to these guidelines or close equivalents should greatly reduce the likelihood of spills, the consequences of a spill must be borne by the violator. The important points to remember are that the topics covered represent major sources of spills which can pollute our waters, and that *all* sources must be controlled. The basic objective is to protect our waterways from spills, not write plans, unless they are effective.

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ANNEX A

Guidelines for Spill Prevention, Containment, and Countermeasure Plan

The SPCC Plan should be a carefully thought-out plan which is technically sound, has the full approval of top management, and is well understood by operating personnel. If the plan calls for additional facilities or procedures not yet fully operational, these items should be discussed in separate paragraphs, preceded and followed by two asterisks; and the details of installation and operational startup should be explained separately.

The completed SPCC Plan should follow the sequence outlined below, and include a discussion of the facility's compliance with the suggested recommendations.

1. Spill History and Notification Procedures

a. Recent history of spills of oil or hazardous materials should be briefly described, particularly as they relate to current practices, or process changes which mitigate against recurrence.

b. In the event of a spill, the procedure should be described for notifying:

a) responsible facility management
b) private mutual aid groups
c) local and State authorities
d) EPA (and/or Coast Guard)
e) outside contractors (for clean up, removal, restoration).

2. *Spill Control*

Recommendations for spill control are listed below.

a. Whenever acids are maintained in bulk storage, an adequate supply of neutralizing material, such as caustic, lime, or shell, should be available on the plant property. The neutralizing agent should be stored as closely as practical to the acid storage area and in sufficient quantity to neutralize the contents of the largest capacity of acid contained in any one storage tank. This supply should be checked periodically to ensure that the material is useable, and that the proper amount is on hand.
b. A supply of personal protective safety equipment, such as rubberized coveralls, rubber boots, safety goggles, gas masks, and rubber gloves should be maintained for immediate use in convenient spill control locations. This supply should be checked periodically to see that the equipment is in good order and useable.
c. When lighter-than-water chemicals are handled and stored within the plant, an adequate length of flotation spill containment boom should be available with suitable means to position the boom strategically and thus confine the spilled material.
d. When oil and/or non-miscible lighter-than-water chemicals are handled and stored within the plant, an adequate amount of absorbent material should be close at hand for treatment.
e. Each handler, transporter, or storer should ascertain the chemical treatment agents that have been approved by the State authorities, and an adequate supply of such agents should be stored at the plant for the treatment of chemical spills.

3. *Plant Drainage*

The following recommendations relative to plant drainage are also made:

a. Drainage from diked storage areas should be valve-restrained to prevent a spill or other excessive leakage of a product into the drainage discharge or in-plant effluent treatment system.
b. Valves used for the drainage of diked areas should, as far as practical, be of manual, open-and-close design. The condition of the retained storm water should be determined before drainage, especially if such drainage of impounded waters goes into water courses and not into waste-water treating plants, as discussed in 6 (c).
c. All plant drainage systems, if possible, should flow into ponds, lagoons, or catchment basins designed to retain materials less dense than water. Consideration should also be given to possible chemical reaction, if spilled chemicals are commingled.
d. If plant drainage is not engineered as above, the final discharge of all in-plant drainage ditches should be equipped with a diversion system that could, in the event of an uncontrolled spill, be returned to the plant for treatment, the objective being to work toward a closed-cycle system.
e. Where drainage waters are chemically treated in more than one treatment unit, natural hydraulic flow should be used. If pump transfer is needed, two "lift" pumps should be provided, and at least one of the pumps should be permanently installed.

4. *Marine Loading/Unloading*

Relative to marine loading/unloading facilities, the requirements and regulations of the Department of Transportation should be met. The following recommendations should be emphasized:

a. On at least an annual basis, all flexible hoselines should be subjected to hydrostatic testing. Inferior or discarded hoses should be removed from the dock area. Consideration should also be given to using hose lines with an outer strain relief braid, or using metal-constructed, articulated-joint transfer lines.
b. When conditions permit, all ships and barges loading or unloading materials lighter-than-water should be effectively boomed in the area of material transfer. When tide and current conditions warrant such protection, "stand-offs" should be used to gain the fullest containment efficiency of the floating boom.
c. Transfer pumps and flange connections should not be positioned directly above the water. When practical, such facilities should be positioned on shore and be confined within a suitable containment curb that will effectively contain material drips and spills.
d. All dock-mounted pumps and pipeline connections should have catch trays positioned under

the potential leak area, and such trays should be emptied and cleaned following each material transfer.

e. Pressure-drop alarm and shut-off systems on the lines leading from the ship or barge should be provided so that losses from a line break will be held to a minimum.

f. Adequate mooring lines forward and aft, and crossed-spring lines should be secured to all ships to ensure a minimum of movement during loading-unloading operations.

g. As far as practical, wooden decked docks with gaps between decking should be avoided as spills can drip between the decking. Preferably, full concrete or seawall-type marine loading-unloading facilities should be used. Such dock areas should be equipped with perimeter containment curbs complete with valve-type drains that can be opened to discharge rainwater and be kept closed to contain spills.

h. Access to and from ships or barges should be such that the crews of the ships and/or barges have no occasion to pass in or around the loading/unloading control area; fenced areas should guide persons safely away from the loading/unloading facility.

i. All terminal flange connections on marine dock facilities should be blanked or capped when not in service.

j. All pump controls on marine docks should be secured in the closed position or electrically isolated when not in service.

k. The practice of loading or unloading a barge or ship when such a barge or ship is tied outboard of another ship should be avoided. The fueling or bunkering of a ship with the fueling barge tied outboard of the other should be avoided. When practical, the fueling ship and the fueling barge should be secured directly to the dock facility, using the marine terminal onshore line connections to transfer fuel or hazardous polluting substances.

l. A direct line of communication, separate from other in-plant or outside telephone lines, should be provided between the marine loading/unloading facility and the immediate tank farm area.

m. "Slop" tanks should be provided at all marine loading/unloading facilities to safely contain the products of flexible hose line draining and, when practical, to contain polluted bilge water discharged from visiting ships and barges. Such tanks should be installed in a fire- and explosion-proof manner with adequate systems to prevent mixing of dangerously incompatible materials.

n. For the prevention of spills during flexible hoseline connection and disconnection, butterfly valves should be installed immediately adjacent to the terminal flange connection. The valves will permit manual opening and closing of the hoseline to retain products that cannot be drained from the line after product transfer.

5. *Tank Car and Tank Truck Loading/Unloading*

Relative to tank car and tank truck loading/unloading procedures, the requirements and regulations of the Department of Transportation should be met. The following recommendations should be emphasized.

a. A system of containment curbs should be used for tank truck unloading areas, using ramps to provide truck access into the confines of the containment curb. The curb enclosure should be designed to hold at least the maximum capacity of any single tank truck loaded or unloaded in the plant.

b. A trenching system should encompass each railroad tank car unloading area. The trench should be designed to carry away any spill to a catchment basin or holding pond, at least equal in capacity to the capacity of the largest tank car loaded or unloaded in the plant.

c. As a fail-safe precaution, an interlocked warning light or physical barrier system, or warning signs, should be provided in loading/unloading areas to prevent vehicular departure before complete disconnect of flexible or fixed transfer lines.

d. Prior to filling and departure of any tank truck, the lowermost drain and all outlets of such vehicles should be closely examined for leakage, and if necessary, tightened, adjusted, or replaced to prevent liquid leakage while in transit.

6. *Bulk Storage Tanks*

Relative to bulk storage tanks, the following recommendations are made:

a. No tank should be used for the storage of oil or hazardous polluting substances, unless its material and construction are compatible with the material stored.

b. All bulk storage tank installations should be planned so that a secondary means of containment is provided for the entire contents of the largest single tank. Dikes, containment curbs, and pits are commonly employed for this purpose, but they may not always be appropriate.

An alternative system would consist of a complete drainage trench enclosure arranged so that a spill could terminate and be safely confirmed in an in-plant catchment basin or holding pond.

c. Drainage of rainwater from the diked area into a storm drain or an effluent discharge that empties into an open water course, lake, or pond, and by-passing the in-plant treatment system may be acceptable if:
   1) the by-pass valve is normally locked closed
   2) thorough analysis of the rain water ensures compliance with applicable water quality standards
   3) the by-pass valve is unlocked, and relocked following drainage under the supervision of responsible management
   4) adequate records are kept of such events

d. The storage tanks located immediately adjacent to the dike itself should be oriented with respect to the dike so that no manholes face the dike. This is considered desirable, so that if a manhole fails, the resulting discharge from a full tank will not be aimed over, or at the dike.

e. If storage tanks located immediately adjacent to the dike itself are equipped with fill lines which enter the tank near the bottom and if the fluid pumped has suspended abrasive material, the discharge into the tank should be on the dike side, discharging against the tank side away from the dike. Alternatively, a baffle plate located inside the tank opposite the pump discharge in the area apt to be abraded, may be provided.

f. Buried storage tanks represent a potential for undetected spills. A buried installation, when required, should be wrapped and coated to retard corrosive action. In addition, the earth should be subjected to electrolytic testing to determine if the tank should be further shielded by a cathodic protection system. Such buried tanks should at least be subjected to regular hydrostatic testing. In lieu of the above, arrangements should be made to expose the outer shell of the tank for external examination at least every five years. A means of conducting regular internal examinations of the tank at five-year intervals should be provided (down-hole television, etc.).

g. Partially buried tanks for the storage of oil or hazardous materials should be avoided, unless the buried section of the shell is adequately coated, since partial burial in damp earth can cause rapid corrosion of metallic surfaces, especially at the earth/air interface.

h. Above-ground tanks, depending on design (floating roof, etc.), should be subjected to integrity testing, either by hydrostatic testing, visual inspection, or by a system of nondestructive shell thickness testing. When the latter system of integrity testing is used, comparison records of shell thickness reduction should be maintained.

i. The foundation and/or supports of all bulk storage tanks should be subjected to at least annual examination by a person with the technical competence to assess the condition of the foundation and/or supports.

j. To control leakage through defective integral heating coils, the following factors should be considered and applied:
   (1) The past life span of internal steam coils should be determined, and a regular system of maintenance and replacement that does not exceed the anticipated life span should be established.
   (2) To reduce failure from corrosive action, prolong life, and reduce replacement costs, the temperature and environment have to be carefully considered when selecting heating coil materials.
   (3) The steam return or exhaust lines from integral heating coils which discharge into an open-water course should be monitored for contamination, or passed through a settling tank, or skimmer, etc.
   (4) The feasibility of installing an external heating system should also be considered.

k. Each bulk storage tank should be externally examined at least once a month. Each inspection should include an examination of seams, rivets, nozzle connections, valves, and pipelines directly connected to the tank.

l. New and old tank installations should, as far as practical, be fail-safe engineered or updated into a fail-safe engineered installation. Consideration should be given to providing the following devices:
   (1) High liquid-level bell or horn alarms with an audio signal at a constantly manned operating or listening station; in smaller plants an audible air vent may suffice;
   (2) Low liquid-level alarms with an audio signal at a constantly manned operating or listening station; such alarms should have a nonbypassing reset device that can be readjusted to a given operating level following tank fill or liquid removal;
   (3) High liquid-level pump cutoff devices set to stop flow at a predetermined tank-content level:

(4) Direct audible or code signal communication between the tank gauger and the pumping station;

(5) At least one fast response system for determining the liquid level of each bulk storage tank such as digital computers, telepulse, or direct vision gauges.

m. "Normal" plant effluent should be constantly monitored by a proven monitoring system, and any deviation from normal should be engineered to activate a visible readout recorder with an audible alarm that can be heard at a constantly manned operating or listening station. If practical, the monitoring device should be designed to operate a bypass to release the effluent discharge into a holding pond;

n. Visible product leaks from tank seams and rivets should be promptly corrected.

o. Tanks should not be used with the knowledge that the "head" or "top" is in a corroded-through condition. Action should be taken to drain such tanks and repair the defective member as promptly as possible.

p. When practical, each bulk storage tank should be lettered (code or otherwise) or color-coded to indicate its chemical content, the Manufacturing Chemists Association or Department of Transportation coding being preferred, and the coding should duplicate those used for chemical transportation identification.

q. The use of wooden tanks should be confined to water storage and should be avoided for liquid chemical storage.

7. *Solid Material Storage Pile and Drum Lots*

a. The open stockpiling of ores, chemicals and minerals should be discontinued. Piles of bulk material should be covered to prevent leaching and run off. If open shed-like structures are used for bulk storage, retention curbing should be provided around the perimeter of the pile, or perimeter drainage trenches should direct runoff into a suitable waste water treatment facility.

b. Bulk storage should not be positioned on the natural earth. Storage pads of concrete or other impervious materials should be used as a base to prevent ground water leaching and percolation into the earth.

c. Metal and fiber containers should be loaded, stored, and unloaded so as to minimize possibility of container damage. The containers should be stored in a covered area, off the ground in a manner which will preclude damage and weathering to the container and subsequent leakage. The area itself should be provided for drainage to a treatment facility in an analogous manner to diked storage tank areas.

d. If some containers contain corrosive substances, these should be stored so that leakage of these substances will not corrode through adjacent containers.

e. All items outlined under this heading should be periodically inspected to insure physical and mechanical integrity of the drainage and containment systems.

8. *Pump and In-Plant Process and Transfer Pipelines*

Recommendations for pump and in-plant process and transfer pipelines are as follows:

a. Each product pipeline should be clearly marked by lettering (coded or otherwise), color banding, or complete color coding to indicate the product transferred therein. The coding should conform with company policy or standard plant practice which, in turn, should conform with state or federal requirements.

b. Each oil or hazardous material product-fill line which enters a tank below the liquid level should have a one-way flow check valve located as closely as possible to the bulk storage tank. In addition to confining the product to the tank, in the event of valve or pipeline failure, the check valve should permit overhaul of the main shut-off valve and should aid in preventing shock loading of the pipeline and valves from a "slug" of the tank content caused by backflow into an empty fill line. As far as practical, the product flow in suction lines should be controlled by use of a positive displacement pump.

c. Buried pipelines should be avoided. However, buried installations should have a protective wrapping and coating and should be cathodically protected if soil conditions warrant. A section of the line should be exposed and inspected annually. This action should be recycled until the entire line has been exposed and examined on a regularly established frequency. An alternative would be the more frequent use of exposable pipe corridors or galleries.

d. When a pipeline is not in service, the terminal connection at the transfer point should be capped or blank-flanged, and marked as to origin.

e. Wood-to-metal should be avoided as a pipeline support since it is apt to retain moisture and cause pipeline corrosion which, when coupled with the abrasive action caused by the pulsating action of the line, could cause line faiure with resulting leakage. Supports should be designed with only a minimum point of surface contact that allows for the pulsating movement (expansion and contraction) of the line (i.e., rollers).

f. All above-ground valves and pipelines should be subjected to a regular monthly inspection at which time the general condition of items, such as flange joints, valve glands and bodies, catch trays, pipeline supports, locking of valves, and metal surfaces, should be assessed.

g. Elevated pipelines should be subjected to constant review to ensure that the height of vehicular traffic granted plant entry does not exceed the lowermost height of the elevated line; gate check-in and in-plant travel routes warrant attention in this respect.

h. As far as practical, all pumps should be located as close as possible to the storage tank.

i. Flapper-type drain valves should not be used to drain diked areas. Such drain valves should be of manual open and close design, and they should be kept in the closed position when not in service. The drain lines from diked areas should drain directly or indirectly into treatment or holding tanks or ponds or catchment basins.

9. *Security*

Relative to security, the following recommendations are made:

a. All plants handling, processing, and storing oil or hazardous materials should be fully fenced, and entrance gates should be locked and/or guarded when the plant is not in production or is unattended.

b. The master flow and drain valves and any other valves that will permit direct outward flow of the tank's content should be securely locked in the closed position when not in use.

c. The starter control on all oil and hazardous material pumps should be secured or electrically isolated in the "off" position when the pumps are in a nonoperating status.

d. The terminal loading/unloading connections of oil and all hazardous material product pipelines should be securely capped or blank-flanged when not in service. This security practice should also apply to pipelines that are emptied of liquid content either by draining or by inert gas pressure.

PREVENTION OF HAZARDOUS MATERIAL SPILLS IN THE TRANSPORTATION INDUSTRY — INTRODUCTORY REMARKS

C. R. BIGELOW
E. I. du Pont de Nemours & Co.

The prevention of hazardous materials spills in transportation is an appropriate topic for this Conference, which is considering the broad subject of control of spills of these materials. In transportation, we now generally consider them to mean those commodities which meet Department of Transportation, including the Coast Guard, definitions for hazardous substances. Some materials which do not meet these criteria also present certain lower-order hazards in transportation, either to personnel, property, or the environment.

Materials classified as hazardous contribute major positive values to the production of useful goods. Industry and the nation's economy are heavily dependent on hazardous materials, and without them, our living costs would be seriously affected. Many innocuous products, several of which are commonplace, are derived from hazardous materials. The steel industry, textiles, plastics, fertilizers, even the space program, require vast amounts of these materials.

Chemical and Engineering News has recently published its list of the top fifty basic chemical materials produced in 1970. The first five on this list, comprising 42% of the total production of 360 billion pounds, meet DOT criteria for hazardous articles and are regulated. Heading this list is sulfuric acid, a mainstay of the chemical and process industries, which is classified a corrosive liquid. Next is anhydrous ammonia, classified a non-flammable compressed gas, important since it is the basic raw material for the tremendous demand for chemical nitrogen.

The next three items on the C&EN list are oxygen, sodium hydroxide and chlorine, respectively. The hazards as well as the importance of chlorine are generally appreciated by almost everyone. Thirty-three of the fifty materials are either now regulated or will be if pending DOT proposals are adopted.

It is not enough to produce these materials safely, efficiently and economically in our manufacturing plants. Huge volumes must be moved across this nation's transportation network every day to meet the needs of our economy and the country's defense. The National Transportation Safety Board has frequently pointed out the large volumes of hazardous commodities which move over the country's highways, railroads, waterways, and the potential problem this represents. Even though transportation experience with such commodities is good, industry recognizes that some materials involve hazards in transportation. However, the immediate direct danger they present is generally limited.

The shipping community has historically placed emphasis on product containment through the use of highly-engineered containers such as steel drums, pressure cylinders, railroad tank cars, etc., and establishment of standards for maintenance of such containers. In many instances, shippers have imposed voluntary restrictions on the transportation of some products which far exceed the requirements of federal, state and local regulations. Shippers can usually exercise control over the selection of transportation mode and routes over which products are moved. Considerable work has been done, both individually by shippers and through trade associations, in developing systems to respond to mishaps involving hazardous materials to insure that proper countermeasures are applied to control the situation. The Manufacturing Chemists Association's

"CHEMTREC" program is an outstanding example of such efforts.

I am sure that most of you are aware that manufacturers are heavily dependent on the common carrier industry—railroads, truckers, barge operators, pipelines, steamship companies, airlines, and others who offer their services for hire to move goods to market. Although the goal of the transportation industry is the same as the shipping community's—safe and efficient movement of goods—its problems are appreciably different. Considering the large volumes moved, the transportation history of regulated commodities has been generally good. However, some accidents have focused attention on the specialized problems of handling emergency situations in which flammable or toxic materials are involved.

Our panel examined the carrier industry's efforts and its problems in preventing hazardous material spills. We were fortunate to have with us an outstanding group of spokesmen for both government and the carrier industry who discussed rail, highway, and marine transportation of hazardous materials. Each panelist is highly qualified to discuss various aspects of the problem and the matter was examined in detail.

METHODS FOR PREVENTION OF SPILLS IN THE MARITIME INDUSTRY—GOVERNMENT CONSIDERATIONS

ALBERT G. STIRLING
Commander, U.S. Coast Guard

The hue and cry abounds throughout the world and particularly this country, "protect the environment, stop pollution." At every occurrence the government agencies are asked "why did you let it happen?" It's easy to demand action and even easier to suggest solutions when one looks only at the symptoms and not the cause. The newspapers abound with stories of opposition to power plants, refineries and terminals, but I have never observed such opposition suggesting they do without air conditioning to reduce their power demands, or stop their water skiing and automobiles so oil is not required.

It is very simple to eliminate water pollution from hazardous substances, just cease moving them by water or using them in areas adjacent to the water.

Simple? Yes! Effective? Yes!
Feasible? No!

This then is the government quandary, how to protect the environment, and strong action is certainly needed, while maintaining the social needs and growth of this country. Although the remaining remarks in this paper are directed to marine operations, it must be remembered that marine operations are but one facet of the total problem. Although the marine industry must resolve its environmental problems, these problems must be placed in perspective with the overall water pollution problem. In other words, we can not afford to expend vast sums correcting recognized problems when their contribution to the total problem is insignificant.

The first order of business in solving any problem is defining the problem. With the broad category "hazardous substances" this is a monumental job. Here the purist can say "any discharge is a bad discharge" and thus all discharges should be banned. Certainly much can be done with closed cycle systems, but what do you suppose would be the impact on the 1972 elections if Congress tomorrow amended the Federal Water Pollution Control Act to require all municipal sewage systems to be closed onto the municipal city water supply? In addition to this type of very practical problem of public education and acceptance is this country's present economic concerns. Are we willing to pay, and pay how much, for clean waters? Thus we must return to our problem definition and determine such things as: what constitutes no discharge; what constitutes a harmful discharge; what changes in the environment are acceptable; what degree of discharge can the waters assimilate without degradation or change; what degree of risk is society willing or should be asked to accept?

These, in my opinion, are the major philosophical considerations which must be made by the government on behalf of the general population. We can, however, agree that there are some known basic problems within the marine industry contributing to water pollution by hazardous substances, and that some form of government control will be forthcoming. This being so, let's turn our attention to some immediate practical problems which, unfortunately, may be no less difficult to resolve than the above cited far-reaching philosophical problems.

The opinions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the commandant or the Coast Guard at large.

As you are all probably aware the existing (January 1972) section 12 of the Federal Water Pollution Control Act, as amended (FWPCA), assigns no responsibility or authority to the President to control pollution from hazardous substances which would be applicable to the marine industry. The pending legislative proposals (here I will refer only to S2770 (Senate Bill) and HR11896 (House Bill) since the others are quite similar), essentially combine the existing sections 11 (oil) and 12 (hazardous polluting substances) into a new section 311. Basically this will provide the same governmental responsibility and authority over hazardous substances which presently apply to oil, with the addition of a penalty for substances which can not be removed if discharged. (Hazardous substances means "any substance designated pursuant to subsection 311 (b)(2) of the act which when discharged in any quantity into or upon the navigible waters , present an imminent and substantial danger to the public health or welfare, including but not limited to, fish, shellfish, wildlife, shorelines, and beaches.") This being so, let me review the existing legislative authority concerning oil and the Coast Guard's existing program for prevention of pollution by oil for potential implications to hazardous substances.

The FWPCA essentially provides the Government with two methods of preventing oil pollution: the use of civil and criminal penalties and the implementation of preventive regulations.

The criminal penalties ($10,000 fine and one year imprisonment) are for failure to report a spill, while the civil penalty ($10,000 fine) is for "knowingly discharging." There is no penalty for an "accidental" spill, however criminal action can be brought under the Refuse Act of 1899. The Coast Guard is defining "knowing discharges" quite broadly. In Coast Guard Law Bulletin 396 the Chief Counsel said, "I am therefore of the opinion that the words 'knowingly discharged' as used in paragraph (5) of subsection 11(b) of the Water Pollution Control Act, as amended, not only includes deliberate, intentional or willful acts or omissions that result in the discharge of oil in violation of the Act but also includes those acts or omissions which, although without actual intent to cause the discharge of oil, are the result of negligence and there is reasonable cause to believe that such act or omission would inevitable or probably result in the discharge of oil because of existing circumstances or conditions. Said in other terms that might have more meaning to the on-scene enforcement officer, it would include any act or lack of action that results in the discharge of oil in violation of the act, which an owner or operator, or his representative or employee, knew or reasonable should have known would occur when considering the existing circumstance and conditions."

The pending house legislation proposes to delete the phrase "knowingly" while the Senate version substitutes "willfully or negligently". Another significant point is that the penalty is applicable only to the owner or operator and not an employee.

The imposition of penalties have certain limitations. It is a deterrant only when it will make the cost of polluting more than the cost of not polluting. The probability of detection of the spill or spill source directly relates to the capability of penalty provisions to protect the environment. The penalty approach probably does not minimize the risk to the environment created by poor procedures or equipment. Further, because of its non-applicability to employees, it does little to influence the attitudes of the personnel directly controlling the operations. (In this latter respect it should be noted that the Coast Guard can take administrative action against the license or document of seamen for their negligent acts). Thus it appears that penalty action has a place in pollution prevention but is not, per se, sufficient.

The other tool mentioned is that of preventative regulations. Regulations of themselves of course accomplish nothing. However, if they are carefully drawn up to provide a basis for equipment and facility inspection and procedures review, a great deal can be done to minimize the spill potential. It has been the opinion of the Coast Guard for some time that our safety inspection procedures for vessels has minimized the U.S. Merchant fleet's contribution to pollution.

Thus the regulations proposed in the Federal Register of 24 December 1971, focus primarily on shore side facilities with some application to vessels in areas not governed by the merchant vessel safety requirements. The principle objective is to insure by a routine inspection program to be carried out by the Coast Guard that facilities are suitably arranged and equipped for their intended operations, and that adequate qualified personnel are on hand to carry out the operations using a previously agreed upon procedure. The method proposed to assure this inspection program is conducted is to require each facility to have an oil transfer permit issued by the Coast Guard. Since each facility is generally unique as to its arrangement and operation, the regulations are quite general and leave considerable discretion to the inspection personnel. This a double edged sword. On one hand it relieves industry of complying with regulations which may not be applicable to a particular operation, on the other it may expose industry to arbitrary requirements imposed by an over zealous inspector.

What is being attempted then in the Coast Guard's approach to oil pollution prevention in marine operations is a balance between punitive measures and operational regulations. Unfortunately there is no data base upon which an analysis can be made to determine which areas should be left to punitive measures and which should be subject to preventive measures. A spill history does not exist and the data presently being developed is biased by the on going pollution prevention measures. Thus the areas subject to regulation have been selected somewhat by "guestimation" based on limited experience, related safety activities, personnel opinion and for good or bad, public opinion.

What then must be the governmental approach to hazrdous substances assuming legislation similar to that pending, is passed. In my opinion great emphasis must be placed upon preventative actions because hazardous substances in general are not removable. It must be recognized that oil with its many favorable characteristics, i.e., distinctive appearance, specific weight less than water, and relatively slight solubility, practically defies existing clean-up technology. The pending legislation recognizes the lack of a clean-up technology for hazardous substances by imposition of a penalty for those substances which can not be removed.

We are fortunate in that the hazard characteristics of most chemicals which are shipped in marine transport have been recognized, and the product containment and handling systems have received considerable design evaluation. However an area which has been totally neglected is that of tank cleaning. It has been accepted practice to discharge the relatively diluted tank washings over board. I doubt that this practice will continue to be accepted. The industry is going to be faced with a major problem in providing shore reception facilities for ballast and tank washings.

Any permit program will be expanded to include hazardous substances. Facilities will be subject not only to periodic inspections but operations will be subject to routine monitoring by Coast Guard personnel. Civil penalty procedures will be used to keep industry aware that cutting corners, violating regulations, or taking chances to expedite an operation is not acceptable nor economical.

As experience is gained and the reporting system develops a data base for analysis, emphasis must be shifted accordingly to provide the most effective program to minimize spills and spill potential.

I presented a paper before the annual National Safety Council meeting in Chicago in October, 1970, suggesting a means of risk analysis. Unfortunately little progress has been made in developing that suggestion or any other method into a useable risk analysis. One significant part of the risk problem is being attacked however. The Committee on Hazardous Materials of the National Academy of Sciences (NAS) under the auspices of the U.S. Coast Guard is developing a water pollution hazard profile for those hazardous substances carried in bulk. This is an extension of the NAS Evaluation of the Hazard of Bulk Water Transportation of Industrial Chemicals, which presently does include aquatic toxicity ratings. However those ratings have some limitation since, at the time of their assignment, water pollution was not considered as significant as it is today. This rerating of products will undoubtedly result in some products being required to be carried in more sophisticated vessels.

In summary then, I believe the government's control of marine transportation must provide the maximum benefit to mankind by a balance between regulations and penalties based upon identified problems and environmentally, socially, and economically feasible solutions. The cure must not be worse than the disease.

METHODS FOR PREVENTION OF SPILLS IN THE MARITIME INDUSTRY — INDUSTRIAL CONSIDERATIONS

H. G. WILLIAMS
The American Waterways Operators, Inc.

The marine industry tanker, barge and terminal operators have made great strides to eliminate spills of oil and hazardous materials.

Various committees of The American Waterways Operators, Inc. have conferred with the United States Coast Guard in an effort to promulgate design, operations and to improve training of tankermen. Admiral Binder and Admiral Rea's staffs have been cooperative in conferring with industry to make the new regulations workable in an attempt to eliminate spills.

Please note the photograph of barge GATCO 102 (Figure 1). After many hours of discussion with the United States Coast Guard and many proposals of retaining bulwarks from 6" high to 36" high around the entire perimeter of the barge, Gatco proceeded to install an 18" high retainer to prevent spills from hose handling, overflow of any tank from gauge opening, leaking pump packing or other causes both mechanical and human failure. This may prevent a chemical spill or spillage of oil or other pollutants, of which we have been advised Manufacturers' Chemist Association that so far there has been tabulated over 6,000 dry, liquid and gas products. E.P.A. or U.S. Coast Guard to date of this writing have not named or listed all of the so-called hazardous materials.

Private, regulated, and unregulated carriers and builders have improved design in hose handling, overflow retaining, alarm, and communications between terminal and tanker personnel to further attempt to eliminate hazardous material spills.

Use of aluminum lightweight and nonsparking butterfly valves at discharge end of connecting hose is now almost universal to prevent spills at disconnect.

Engineering and design we can do.
E.P.A. and U.S. Coast Guard requirements we can meet, and continue to operate.

The AWO Board of Directors at a meeting in Tampa, Florida on December 1, expressed deep concern over the effect pollution control regulations and proposed legislation is having and will potentially have on the barge and towing industry.

Discussion of specific matters under consideration with respect to this concerned H.R. 11896 and S.2770, omnibus amendments to the Federal Water Pollution Control Act which are now pending before the Congress and which will seriously affect the industry. The Senate has passed S.2770. Among other things, the bill would impose a severe penalty for the spillage of unremovable hazardous substances. The penalty would be $5,000 per barrel or $50,000 per incident, whichever is the greater. The House bill, H.R. 11896, which has been introduced under the sponsorship of all members of the Public Works Committee, proposes a different penalty for unremovable hazardous substances spilled. The House bill penalty would be up to $100 per gross ton of the vessel spilling the substance or $14,000,000, with the penalty to be judged on the toxicity, degradability and disposal characteristics of the substance. The penalty in the Senate bill is purposely aimed at stopping the movement by water of certain so-called hazardous substances. The House bill penalty proposal is generally considered acceptable.

Because of great concern with the harshness of pollution control regulations and proposed laws,

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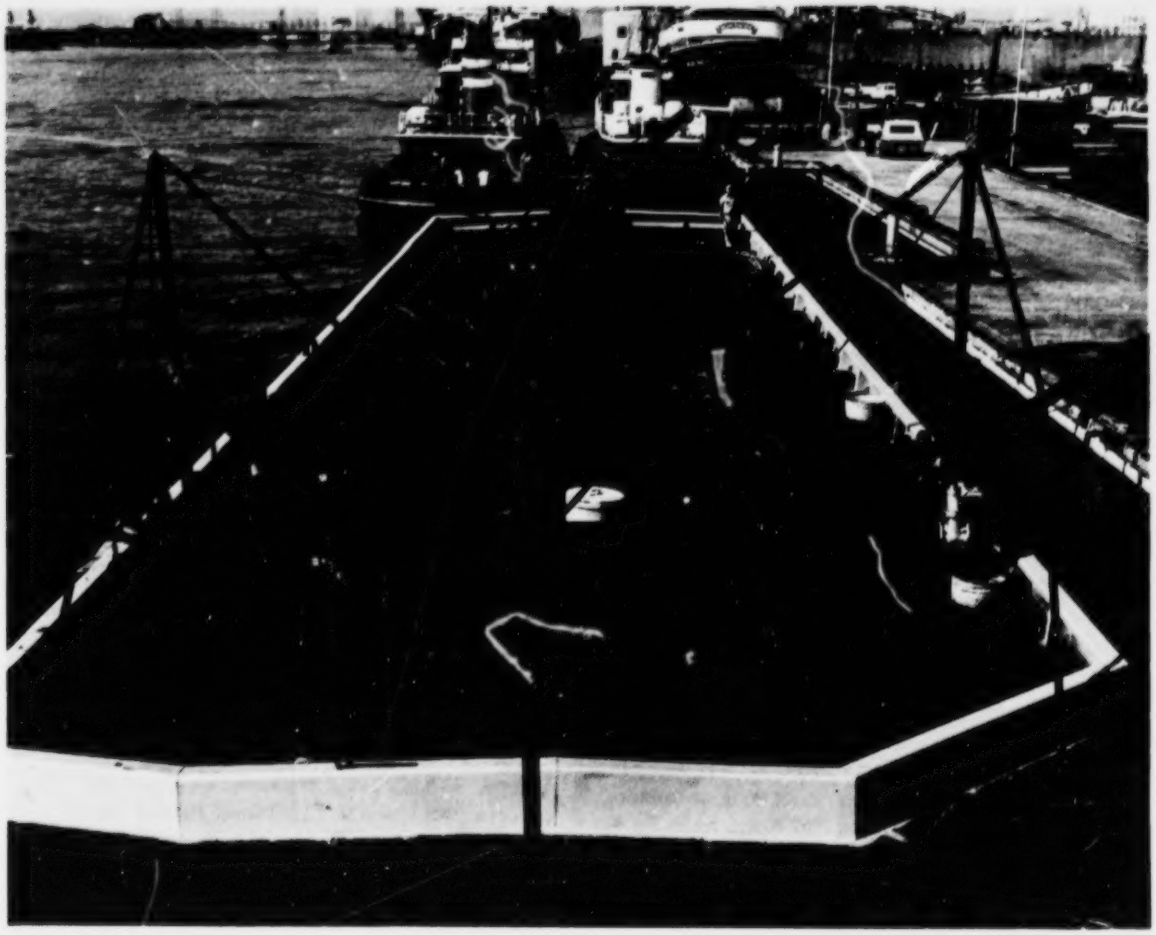

Figure 1

the AWO Public Relations Committee plans to develop, at the direction of the Board, written materials for general distribution showing the amount of polluting substances being transported and the relative safety of such movements by water as compared to alternative means.

Concern was also expressed in the Board meeting with certain anticipated provisions of the pollution control regulations which the Coast Guard is working on now and which are expected to be issued in rulemaking form soon. Members of the Association are being urged to examine these proposed regulations as soon as they are published and prepare comments to the Coast Guard.

With reference to cost of attempting to eliminate other hazardous material spills, the Nixon Administration believes the cost too high. In December, 1971, three of the Administration's top policy makers went before the House Public Works Committee and said both the Senate-passed legislation, S.2770, and the House committee's draft measures, H.R. 11895 and H.R. 11896, were too costly and incorporate perhaps unattainable goals.

The Administration's witnesses were Russell E. Train, chairman of the President's Council on Environmental Quality, William D. Ruckelshaus, Administrator, Environmental Protection Agency, and Paul W. McCracken, chairman, the President's Council of Economic Advisors.

The four days of hearings were sought by the Administration so it could voice its objections to certain provisions of Senator Muskie's omnibus water pollution control bill, S.2770, which the Senate approved unanimously last month. The Administration witnesses were among 51 persons who testified that week.

The Administration witnesses characterized this goal as impractical and unwise. "If we make false promises which we can't fulfill, we may find we have lost the strong support we have now from an overwhelming majority of our citizens," Mr. Ruckelshaus said.

The Administration witnesses said that while they support the general goals of the Senate and House bills, they felt it would be economically unsound to abandon the present method of controlling pollution which relies on the states, with Federal approval, to set water quality standards.

Mr. McCracken estimated the cost of removing 85 percent to 90 percent of water pollutants at an aggregate outlay of about $60 billion with total removal cost as much as $200 billion.

The Administration witnesses endorsed the requirement in the proposed legislation that Federal and state authorities be empowered to require industries to install the "best practicable technology" in controlling water pollution by the year 1976.

I quote Admiral Bender's opinion as set forth in a letter of July 20, 1971, to Honorable Ancher Nelsen, House of Representatives, as follows: "It was recognized that the reflection of the cost in the cost of goods may result in some products becoming non-competitive price-wise due to their high pollution risks or the competitive positions of one mode of transportation shifting with respect to others in the movement of high risk products. This may be desirable from a national viewpoint if we do in fact want to maintain the ability to transport and use products while at the same time maintaining a minimum risk of pollution."

The industry believes and suggests that the Committee consider a penalty based on actual damage caused by the spillage of any hazardous polluting substance which cannot be removed, with such penalty to be determined by the Administrator of the Environmental Protection Agency based on established facts of damage to the environment, to marine life, and such other damages as may be assessable. This is the most reasonable approach to the problem and one that should satisfy the objectives of pollution prevention from such substances moving in marine transportation. Actually no factual assessment of damage or potential damage to the environment has been made in the case of spillages in water of certain substances generally considered hazardous. As a starting point to establish a realistic deterrent to the spillage of hazardous polluting substances which cannot be removed, a penalty based on actual damages not to exceed $100 per barrell or $50,000 whichever is less would certainly be more desirable than anything else from the standpoint of marine transportation and should serve the purpose of pollution control for such circumstances, at least initially until we have a better assessment of the problem. Fines will not eliminate spills, research development, training and precaution will!!

However, after all of the above, under the Refuse Act the operator may be fined through civil action by the Justice Department. *If the severe penalties in proposed legislation and the double jeopardy laws are allowed to continue, there will be little if any so called "hazardous materials" transported by "for hire" marine contractors.*

GOVERNMENTAL CONSIDERATIONS ON METHODS FOR PREVENTION OF SPILLS IN THE RAIL TRANSPORTATION OF HAZARDOUS MATERIALS

QUENTIN H. BANKS
Department of Transportation

The Regulations promulgated by the Federal Railroad Administration endeavor to prevent accidents and reduce the impact of those that occur. The best method of preventing a hazardous materials spill is to prevent the accident which causes the spill. The Federal Railroad Administration is presently developing safety standards covering track and equipment which will reduce the number and the severity of railroad accidents.

Our Hazardous Materials Regulations, which are found in Title 49, Parts 170-179 of the Code of Federal Regulations, likewise promote the reduction in the number of hazardous materials spills and their severity. Tank cars transporting hazardous articles are required to be carefully inspected before being accepted by the carrier and by carriers at each interchange point. Shippers are required to utilize containers which are specifically specified to achieve an adequate level of containment. These containers are required to be physically tested so as to demonstrate that they are leak tight and that they will withstand specified accident conditions. Carriers have specific handling rules which require prompt movement of cars laden with hazardous materials, and there are many other similar safety requirements contained in our Hazardous Materials Regulations. The primary goal of these requirements is to prevent accidents due to leakage or other transport incident. We believe that if we can retain the product within the container, the overall risk to the public in the event of a derailment or other railroad accident will be quite low.

Other provisions of our Hazardous Materials Regulations seek to reduce the severity of spills of hazardous materials. Individual packages of hazardous materials have a limitation upon their total volume, tank cars have a gross weight and volume limitation, and certain chemicals are further restricted as to the total quantity that can be shipped in bulk. All railroad cars transporting hazardous articles are required to be placarded with a specific sign that indicates the name of the dangerous commodity, and the conductor of the train must have a written document in his possession which describes the name of the article, its hazard classification, the amount contained in the car, and the car number. This information is to be furnished to fire, safety and public health personnel so as to assist them in performing their functions and keeping contamination and loss at a minimum.

We constantly review our hazardous classification and packaging requirements to assure that we are imposing the proper requirement to those items which cause significant public hazard. To date, our primary concern has been with chemicals which endanger people and property due to contact, fire, or explosion, rather than to chemicals which cause overall damage to the environment due to spillage. By this, I mean that we are concerned with gasoline because of its extreme flammability and we do not currently regulate rail shipments of fuel oil because fuel oil is much less likely to catch fire; we have not been considering the long term impact of spills. The Department is re-evaluating its thinking on this

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matter. Current Notices of Proposed Rule Making suggest that many additional chemicals will become regulated as hazardous materials within the next few years. Environmental impact damage is being incorporated, to a greater degree in these proposals.

I have just high-lighted a couple of considerations that we in the Federal Railroad Administration have given and are giving to methods of preventing spills of hazardous materials in rail transportation. Our efforts along with the efforts made by the carrier and shipper industries will reduce the number of hazardous materials incidents and will reduce the severity of those which do occur.

METHODS FOR PREVENTION OF SPILLS IN THE RAIL TRANSPORTATION OF HAZARDOUS MATERIALS

J. J. O'DRISCOLL
Southern Railway System

As Alvin Toffler says repeatedly in his current best selling book, *Future Shock*—"We are in a 'Revolution of Change'—in all areas of society and our environment." "Evolution" no longer suffices to properly describe the rapid developments and changes occurring in all areas of our lives. Technology in it's broadest meaning is carrying us forward at a fantastic speed. This "revolution" carries significant effects and demands for improvements in all our activities of living and this is certainly true in the area of Transportation and particularly the transportation of Hazardous Materials. The transportation of Hazardous Materials by rail and other modes is certainly in a "revolution of change."

We on Southern have been very much involved in the "Spill" problem. "Spills" to us have a very significant meaning in rail transportation.

We have been working on Southern Railway to prevent spills in all our activities by eliminating the causes of spills in any and all ways we can. Southern's Management became concerned about the growing number and quantities of hazardous materials carried on the railroad several years ago. A complete reorganization and upgrading of our Safety Department was accomplished in August, 1968, which included the establishment of a Hazardous Materials Section. Duties assigned this section included the development of an Emergency Action Plan for incidents involving hazardous materials, establishment and equipping of a "Go-Team" of trained personnel for handling hazardous materials incidents and incidents that pose a threat to the environment, either our own or the public's.

Analysis of our experience over the past two years will give you some idea of the scope of our problem, and the reason for our plans for prevention, and our plans for controlling any incidents we are involved in. I will cover the highlights now.

In 1970, we had *158* cars of hazardous materials involved in incidents of all types; *31* were involved in derailments in which *6* spilled their contents due to being ruptured and half of those (3) burned. In regular operations there were *67* spills or leaks due to a variety of causes for a total of *73* spills in 1970. In 1971, the figures were a total of *65* incidents, *20* cars involved in derailments, *2* of which spilled their contents due to being ruptured and both burned. In regular operations there were *25* spills or leaks due to a variety of causes for a total of *33* spills in 1971, a remarkable improvement, we believe. Incidentally, the major types of materials involved were the same as found in DOT's 1971 report; first, flammable liquids; second, corrosive liquids; and a weak third, poisonous liquids or solids, Class "B"—a real pollution threat.

To identify the *problem* and to learn the real causes of spills in Rail Transportation, I would first like to put the situation that exists in a more realistic perspective.

During the last few years there has been a great deal of misinformation about the size of the accident/catastrophe problem in Railroad operations. These statements and articles have been published by supposedly reputable persons. They have done a disservice to the Railroad Industry and the general public as well. The railroads haul the freight—41% of all freight goes by rail and a larger percentage of hazardous materials moves by rail. There were over two million carloads of chemical and petroleum products handled in 1970. Many of these products, while classified as hazardous materials, are essential to the working or our society as we know it today. We believe the railroads are the safest mode of transportation for the majority of these essential hazardous materials.

The accident experience over the last thirty years in the rail transportation of millions of tons of hazardous materials yearly has resulted in a fatality rate of *1.1* persons per year. In the 1960's there were 11 persons killed for a fatality rate of *1.1* per year. On the highways, there have been over *50,000* killed each year since 1965. While these figures help define the problem, I do not want to suggest that we do not have a problem—we do and it is growing.

The "Revolution" is causing a growth in the chemical industry alone of *8%* a year, and the numbers of new materials invented and introduced into our society yearly are amazing—many of which are "Hazardous"—they have to be to be useful.

The first six month's report of Hazardous Materials Incidents by the Office of Hazardous Materials had a total of *884* incidents, of which *731* were due to the three leading classes: *390*, flammable liquids; *242*, corrosive liquids; and *99*, Class "B" poisons, liquid or solid. While this report covers all modes of transportation, it does give us some idea of the experience in transportation. In view of the "growth" evident in all areas—these figures will also grow unless some real improvements are made in transportation operations. We intend to make those improvements.

Hazardous materials "spills" in Rail Transportation present a very unique problem in that:

1. Amounts of materials spilled can vary from teacups to tank cars or several tank cars, each of which can range from 8,000 to 48,000 gallons capacity.

2. Spills can involve any of thousands of hazardous materials carried by rail. A single material or a variety of materials, sometimes of unknown nature, can be involved and mixtures occasionally occur, particularly in derailments.

3. The location of the incident can be anywhere on the System, in yards, terminals, industry tracks, or on line of road, in towns, cities or open country. Fortunately, major spills caused by derailments are usually in open country on line of road and incidentally, it seems they always occur at 1:00 a.m. during a heavy downpour and on a weekend.

4. When they do occur in remote areas access can be a problem, and getting personnel to the site rapidly is a challenge. Charter flights are frequently used, in fact, my last two visits to Houston were terminated in the early hours.

5. In derailments a unique hazard can occur, a small leak of flammable compressed gas or liquid, if ignited, can lead to a catastrophic rupture of adjacent cars such as occurred near here in October, resulting in an instantaneous "spill" in the form of a 1,000 foot fireball.

While spill situations in railroad transportation are unique, their prevention and proper control measures, when they do occur, are of necessity unique, and in some cases quite unusual.

"*Prevention*" is certainly the key word in handling spills in rail transportation, as you can see from my brief explanation of the circumstances that can be and usually are involved in major spills on the railroad.

Analysis of our experience has shown that the causes of spills vary considerably and fall into several major categories. We and our customers are in a joint operation, and improvements must be made in both areas.

1. Railroad Operations—which include:
   a. Derailments (Numerous causes)
   b. High speed impacts—slack action
   c. Humping and switching operations
   d. Normal railroad transportation environment
2. Shippers Operations—which include:
   a. Inadequate containers or cars
   b. Improper closure of fittings, caps and plugs
   c. Overloading—liquid full
   d. Inadequate blocking and bracing—poor loading

On Southern we have concentrated on improving our property, tracks, equipment, and train operations as well as in hump yards and switching. These efforts are bearing fruit and our derailments have decreased steadily over the last three years while our tonnage has gone up. Investments in track improvements and equipment have steadily increased over the last several years, and our operating practices have been tightened greatly. Our "spill" experience and losses to freight claims are reducing rapidly—obviously we are moving in the right direction.

In working with our customers—the shippers—we have visited their plants, worked with their people at the loading docks and warehouses. We have given the facts of what can be done to prevent these incidents, and, in practically all cases, they have cooperated willingly. We feel we are both in the boat together and mutual cooperation is the only answer. We believe the facts speak for themselves.

"Prevention" is certainly the answer to the spill problem; however, while we feel there is a great deal of room for improvement, we must admit that "spills," like sin, will continue to occur. We have developed a second line of defense in our Emergency Action Plan for Handling Hazardous Materials Incidents", of which we are quite proud—Southern was the first railroad in the country to develop such a plan and today several other carriers have developed similar programs.

METHODS FOR PREVENTION OF SPILLS IN THE TRUCK TRANSPORTATION OF HAZARDOUS MATERIALS*

CHARLES E. RAMSEY
U.S. Department of Transportation
Bureau of Motor Carrier Safety

Congratulations to those of you in the petroleum industry—those of you in the chemical industry—those of you in regulatory functions—those of you in research and education—and interested private citizens for your concern and understanding of the common problems facing the public, industry, and Government.

It is good that, together, we can explore this important subject of hazardous material spills. For, in the final analysis, we are all interested in the same results, that being a reduction in the unnecessary release of hazardous materials in order to better protect our environment and the citizens of this fine country we live in.

What is the Bureau of Motor Carrier Safety's role in the problem of hazardous material spills? This could best be explained by a statement of our mission which is to administer a program to reduce the occurrence of commercial vehicle collisions; to decrease fatalities, injuries and property losses due to commercial motor carrier involvement; and to make a meaningful contribution to the reduction of casualties and economic loss in the overall motor vehicle safety effort.

The Bureau is responsible for the development and revision of rules and regulations governing the qualifications and hours of service of motor carrier employees; the safe operation and maintenance of motor carrier vehicles; the safe transportation of cargo, bus passengers, and migratory workers; the reporting and recording of accidents; and the safety of drivers.

The Bureau is responsible for the development and revision of rules and regulations governing the marking, packaging, loading and transportation of explosives and other dangerous articles on the Nation's highways, including specifications for shipping containers and cargo tanks used for the transportation of dangerous articles by highway.

Our relatively small Bureau has a Hazardous Materials Specialist in each of our nine regional offices. These specialized men are to keep abreast of the problem areas involving hazardous material shippers and carriers domiciled in their assigned region.

The chemical population explosion continues all around us—so much that it is almost impossible to keep hazardous material reference guides and manuals currently updated. Similarly, use of large groups of hazardous materials has grown over the past 20 years.

The properties of corrosives, combustible materials, radioactive substances, cryogenic materials, new and more lethal insecticides and other hazardous materials are of direct concern to the motor carriers transporting these products, as well as the emergency response personnel.

In this modern age of mobility, the problems of transportation spills are ever increasing. It is estimated that 1 out of every 10 commercial trucks rolling on our Nation's highways carries some quatity of hazardous material as its cargo. It might be a 5-gallon container of liquid insecticide or it could be a cargo tank vehicle loaded with a highly flammable gas. A spill from the 5-gallon container of insecticide could be as catastrophic as the explosion of a cargo tank loaded with LPG. A few years ago, in old Mexico, a truck was transporting a liquid insecticide, (parathion mixture) class B poison, in the same vehicle with foodstuffs. During the course of transportation some of the insecticide leaked from a container and contaminated bags of sugar. When the contaminated sugar was used by a bakery, death resulted for 13 school children. As a result of this tragic incident, the U.S. Department of Transportation initiated emergency rule-making action prohibiting the transportation of class B poisons in the same vehicle with foodstuffs, feeds, or any other material intended for consumption by humans or animals. Let's face it—the transportation of hazardous materials can be a catastrophy in the making if necessary precautions are not taken to prevent spillage.

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*The views expressed in this paper are those of the author and do not necessarily represent the position of the Federal Highway Administration or the Department of Transportation.

Incidents involving hazardous materials have been a matter of grave concern to the Bureau of Motor Carrier Safety for years. Prior to January 1, 1971, there were several regulations requiring submission of hazardous materials incident reports which were designed to meet the requirements of individual transportation modes. These reporting systems were such that integration of individual data could not be accomplished. One such outstanding problem was the lack of accurate identification of the container and cause of failure. Effective January 1, 1971, all carriers are required to report to the Secretary, Hazardous Materials Regulations Board, incidents involving the unintentional release of hazardous materials. These incidents are reported on the "Hazardous Materials Incident Report," Form DOT F5800.1, and the reports are reviewed in an attempt to identify trends involving spillages, such as container failure, commodity experience and other hazardous materials transportation problem areas. This new reporting system has provided an excellent input of material to evaluate proposed rule making. A summary of these incident reports is included as Appendix "A."

A recent study of hazardous materials incident reports revealed that numerous gasoline spillages are occurring as a result of cargo tanks and storage tanks overflowing during loading and unloading procedures. A safety bulletin was prepared by the Bureau and distributed throughout the United States to express our concern with preventable spillages. The safety bulletin is included as Appendix "B."

With the cooperation of the Office of Hazardous Materials, numerous hazardous materials seminars have been presented in an attempt to better educate the shipping public, emergency personnel, and regulatory personnel involved in hazardous materials transportation. Through these educational efforts, the Bureau hopes that much progress has been made towards reducing hazardous material spillages. At least we are all becoming more aware of the dangers surrounding hazardous material spills. In closing, I would like to pose a hypothetical transportation spillage accident for your indulgence. Suppose you are in top management of a motor carrier and the situation as follows presents itself:

Transportation Spillage Accident

You are in your office performing routine duties when you receive a telephone call from your terminal manager in Dallas, Texas. He relates the following incident:

A tractor-trailer vehicle dispatched from Nashville, Tennessee, arrived here a few minutes ago with liquid dripping through the bed of the semitrailer. This was discovered by a mechanic who was about to repair the brakes. The trailer was not yet unloaded. The mechanic wiped some of the liquid on his finger to smell and taste it. He then told the dock foreman about the leak.

The dock foreman checked the bills that had just arrived via air mail and noted that 2,000 pounds of "liquid insecticide" was in the shipment. No shipping papers accompanied the vehicle or drivers while en route from Tennessee to Texas. The trailer was then brought to the dock for unloading. When the rear door of the trailer was opened, a disagreeable odor immediately spread throughout the dock area and front offices. The trailer was then moved to a far corner of the lot to air out.

The terminal manager stated that the shipment also contained books, breadsticks, chewing tobacco, drugs, bolts, carpets and several other items, but no other hazardous materials. He also added that the shipment had been scheduled for a change of drivers at Texarkana, Arkansas, and that the second driver did not notice any leakage during his part of the trip. There was a "Dangerous" placard on the rear of the trailer.

One of the cans, visible from where the leak appeared to be coming, revealed the contents to be "Parathion" and was labeled with a diamond-shaped poison label. Underneath the leaking drum a piece of broken metal was found. During the unloading of the trailer, none of the remaining 5-gallon drums of parathion mixture was observed to be damaged. Three of the men who unloaded the trailer complained of dizziness, slight nausea, and a mild headache. After resting in the fresh air, however, these symptoms disappeared in a few minutes.

The terminal manager requests your assistance at this point.

1. What is your first concern at this point?
2. Who should be notified about the spillage?
3. What precautions should have been taken during the unloading of the trailer?
4. Besides the commodities in this shipment, what has been contaminated and what should be done?
5. What should be done with the contaminated goods?
6. How could this accident have been avoided?
7. Are there any apparent violations of the Hazardous Materials Regulations?

Answers to Questions Proposed In Transportation Spillage Accident

1. The mechanic is the first concern at this point because he is known to have been directly exposed to parathion. He should have been sent to a hospital for observation and a medical examination. If symptoms appear, treatment for parathion poisoning should be administered.

The *three workmen* unloading the trailer had temporary illness, probably due to the noxious odors of parathion liquid concentrate in a partially closed environment. However, if any doubt exists, a physical examination and chlineterase test can be performed.

The initial driver should also be contacted to find out if he had any exposure to the parathion—this could be done through the trucking company involved. Generally, the first concern in an accident of this type is to find out who might have been exposed, and to prevent any further human exposure.

2. a. Chemtrec 800-424-9300 (Chemical Transportation Emergency Center—for immediate guidance by telephone on procedures to follow in cases of spills.)
   b. State Health Department.
   c. Alert local Poison Control Center for possible parathion poisoning.
   d. Shipper of the Chemical—decontamination team should be contacted.
   e. Department of Transportation—Telephone Number is 202—426-1830.
   f. Food and Drug Administration.

3. Protective clothing, such as rubber gloves, should be a minimum amount of equipment worn by anyone unloading goods from the trailer. Other protective clothing, such as rubber pants, jacket and boots should be used if indicated. A shower following the unloading should be demanded instantly.

All contaminated goods should be placed in an area by themselves and placed in such a place where they will not be shipped on to the consignee. All known contaminated goods should be disposed of (see #5). Suspected items should be sampled by analytical methods and considered contaminated until proven otherwise.

4. The trailer bed—decontaminated or replaced. Since this was a concentrated insecticide (95%), complete replacement of the wooden bed and sides is recommended.

Dock Area—scrubbed down with bleach and detergents since Parathion is rapidly hydrolyzed in alkaline solutions.

5. Although there is no good way to dispose of pesticides and contaminated goods, items that are burnable should be taken to an incinerator in which the vapor will not expose humans. Other items should be taken to a sanitary landfill that does not drain directly into a watershed and buried.

6. The piece of metal on the bed of the trailer could have been swept out prior to loading. However, a more complete control measure would be to place the drums on pallets.

7. a. Shipping papers were not in the possession of drivers during the trip.
   b. Class "B" poisons were transported with foodstuffs.
   c. Improper placarding.

APPENDIX "A"

Six Months of Incident Reporting

A summary of Hazardous Materials Incident Reports (DOT Form F5800.1) received by the Secretary, Hazardous Materials Regulations Board, during the first 6 months of 1971, shows that 193 carriers submitted a total of 881 hazardous material incident reports. A few were submitted by other than carriers, but these were not separately included in the tally since they duplicated the involved carrier's report of the same incident.

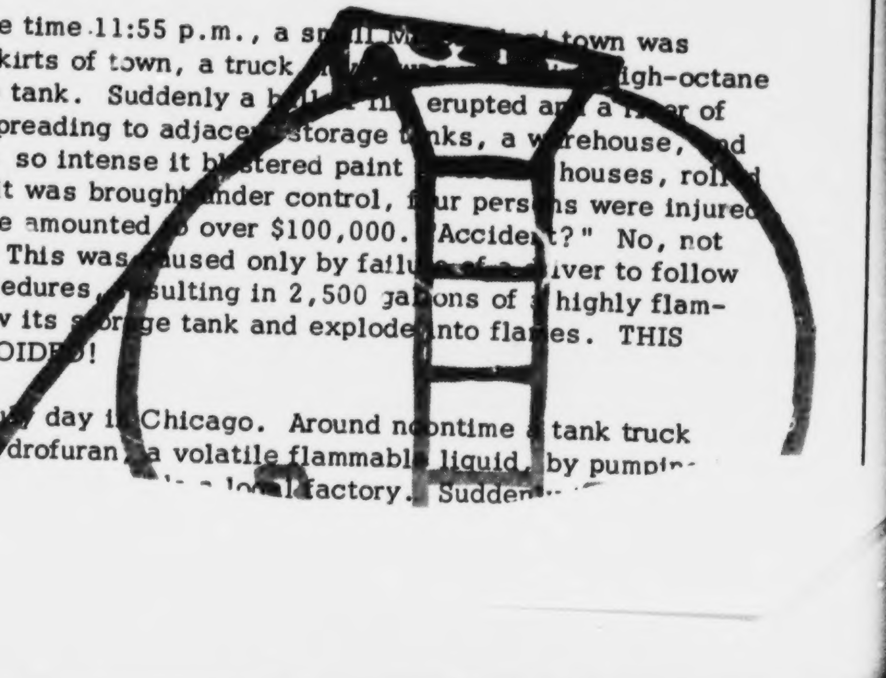
The following table shows the "classification" breakdown of the reports. A few reports did not identify the commodity or investigation revealed it was not subject to the hazardous materials regulations.

Classification Group	Jan.	Feb.	Mar.	April	May	June	Total
Flammable liquid	28	55	83	62	78	84	390
Flammable solid	0	3	3	1	2	3	12
Oxidizing material	0	5	16	6	6	6	39
Corrosive liquid	22	35	50	37	37	61	242
Nonflammable compressed gas	3	3	8	5	3	12	34
Flammable compressed gas	3	1	10	7	5	3	29
Poison gas or liquid, Class A	0	0	0	0	0	0	0
Poisonous liquid or solid, Class B	8	9	19	18	20	25	99
Tear gas, Class C	0	0	0	0	0	0	0
Radioactive materials	0	1	1	0	1	0	3
Class A explosives	0	1	0	0	2	7	10
Class B explosives	0	2	0	1	0	3	6
Class C explosives	0	1	4	0	1	1	7
Unknown, not identified or determined non-hazardous	0	1	5	3	1	3	13
Total	64	117	199	140	154	210	884

APPENDIX "B"

ON GUARD
BUREAU O
MOTO
CARRIE
SAFETY
BULLETI
VOL. 3 NO. 2
WASHINGTON, D.C.

SPILLS KILL



The night was still, the time 11:55 p.m., a small M[illegible] town was sleeping. On the outskirts of town, a truck [illegible] high-octane gasoline into a storage tank. Suddenly a b[illegible] erupted and a r[illegible]er of flames began rapidly spreading to adjacent storage tanks, a warehouse, and plant facilities. Heat, so intense it blistered paint [illegible] houses, rolled over the area. Before it was brought under control, four persons were injured and the property damage amounted to over $100,000. "Accident?" No, not according to Webster. This was caused only by failure of a driver to follow established safety procedures, resulting in 2,500 gallons of a highly flammable liquid to overflow its storage tank and explode into flames. THIS SHOULD HAVE BEEN AVOIDED!

It was a typically hot July day in Chicago. Around noontime a tank truck began unloading Tetrahydrofuran, a volatile flammable liquid, by pumping directly into a [illegible] a local factory. Sudden[illegible]

THE EXPOSURE OF THE TANK TRUCK CARRIER TO HAZARDOUS MATERIALS SPILLS

CLIFFORD J. HARVISON
National Tank Truck Carriers, Inc.

I would like to make it clear that the views expressed from this podium are my own and not, necessarily, those of the individual for-hire tank truck carriers; although I am (personally) confident that my expressions would bring at the very least a "consensus" of agreement among the carriers I am paid to represent.

Now, a couple of quick notes on "what is" the for-hire tank truck industry. This segment of trucking is a specialized group of approximately 400 interstate carriers dealing, primarily, in the transportation of commodities in bulk in tank motor vehicles. Additionally, there is a large number of smaller intrastate carriers who perform the same services. Please keep in mind, however, that NTTC does *not* represent the private carrier.

Just one sidelight. When I was first contacted about this Conference, I was informed that the title of the session was to be "The National Conference on the *Prevention* of Hazardous Material Spills." My first thought was . . . "Good God, another 'pie-in-the-sky' meeting on how to achieve the impossible—namely, 'prevention'." I was more than relieved to be informed there was the substitution of the word "control" for "prevention" in the title of the Conference, because of the implied recognition of the fact that when one deals with any combination of machines and humans—control of incidents is the best that can be hoped for.

So, now that I have established a premise—let's look at some facts of life: a(The transportation of all types of commodities—via the highway mode can be expected to increase; b) The nature of tank truck operation presumes utilization of routes which are contiguous to populated areas; and, c) Tank truck companies are operated and managed by men whose speciality is transportation—they are not chemists or environmentalists (and they should not be expected to be so).

Few people recognize that our carriers are already subject to the rigid jurisdiction of the U.S. Department of Transportation with respect to the transportation of dangerous commodities. Already, the DOT regulations specify, for instance, certain manufacturing criteria and specifications for the tank vehicles involved in these movements.

The principle thrust of these tank vehicle specifications is aimed at "product retention" in the event of an accident. In other words, each tank hauling hazardous materials must be designed and manufactured to specifications which will provide the "best probability" of keeping the product inside the tank in the event of a collision or single vehicle accident. Make no mistakes about it, the DOT specifications entertain the economic realities of tank truck transportation to the point that our industry does have gross weight limitations.

Yet another role of the Department of Transportation is its process of "hazard classification" by which certain products are deemed to be "flammable", "corrosive", "compressed gases", etc.

Now, we are beginning to get down to the "rub of the grain", as far as this Conference is concerned.

In other words, the present "hazard" classification deals exclusively with the effect of release of the commodity directly on humans who happen to be in the vicinity of the accidental release.

Today, the environmentalist is asking, " . . . what about the indirect consequences?" Let me illustrate.

Presently, the Department of Transportation considers "edible oil" a nondangerous commodity, and therefore exempts it from its regulatory purview.

But, what happens when a carrier dumps a load of this commodity into a stream which leads into a city reservoir? The results could be a severe problem of water purification for the city involved. The oily residue might clog filtration systems, kill bacteria and produce any number of side effects which (though considered "minor" by the transportation expert) might be considered "catastrophic" by the environmentalist.

There are other examples which I could give here—especially those instances in which two (or more) non-dangerous commodities are accidentally mixed, producing highly hazardous reactions.

What's to be done to "control" this possibility? I say a better, "more controlled" method of communication between shipper, carrier and emergency personnel.

The tank truck carrier may transport, annually, thousands of different commodities. He cannot be expected to know and appreciate the potential environmental impact of each.

He should be confident, however, that there is a source of information for him—should an accident or incident occur. This should be the manufacturer (not necessarily the shipper) of the product.

That manufacturer should be bound to make specific determinations as to the hazards presented by transportation of his product—including environmental hazards and make those hazards available to the carrier and emergency personnel. This is no new idea—several chemical shippers and manufacturers do this, today, through the Manufacturing Chemists Association and their "CHEMTREC" program.

This is an excellent *voluntary* program, but it does involve just the big manufacturers. There are thousands of other suppliers who don't participate in MCA's programs, but who, in any given instance, are the number one program? My point is that if "systemized" information cannot be given "voluntarily", it might have to be done by preemptive Federal legislation.

We must establish the premise that it is the manufacturer of the product who is the best person to know its physical properties, and thus, it is his responsibility to pass such information on to the public.

THE NATIONAL CONTINGENCY PLAN—PRESENT AND FUTURE

RICHARD E. HESS
Environmental Protection Agency

INTRODUCTION

The key to protecting the environment from spills of hazardous substances is multifaceted in that it involves design, engineering and construction of facilities and equipment to *prevent spills*; stockpiles of equipment and available trained manpower to *clean up* spills; and *contingency plans* to insure prompt and effective implementation of countermeasures to mitigate the effects of spills.

The purpose of this paper is to discuss the National Contingency Plan, its history, its basis, its functions, and how *its provisions relate specifically to spills of hazardous substances.*

The National Contingency Plan has its roots in oil, having been developed initially in 1968, after the TORREY CANYON and OCEAN EAGLE tanker accidents. Additional impetus for establishing a National basis for responding to spills stemmed from the following incident:

> On January 1, 1968, at about 9:30 p.m., two trains including five tank cars carrying chemicals, crashed near Dunreith, Indiana.* The tank cars, each containing 20,000 gallons of material, carried the following: two-acetone cyanohydrin; and one each of vinyl chloride, ethylene oxide and methyl methacrylate. Explosion and fire, with the evolution of toxic gases, followed immediately after the accident, and townspeople were evacuated. About noon, on January 2, motorists reported noticing dead cattle and fish along Buck Creek, south of and downstream from Dunreith. This confirmed fears that, although there appeared to be no outlet from the wreck site to the stream, chemicals from the tank cars entered Buck Creek. During the investigations of the stream in the vicinity of the fish and animal kill, the characteristic odor of cyanide in the water gave a clue to at least one cause of the mortalities. Analysis showed a maximum concentration of over 400 mg/1 cyanide into the Creek.
>
> After locating the slug of pollutants containing approximately 1600 lbs cyanide, and following its progress, the decision was made by Indiana State Board of Health to treat the East fork of the White River upstream from the City of Seymore, which is the first municipality to take its water from the River. Accordingly, 6200 lbs of calcium hypochlorite were added to the Big Blue River between the evening of January 5 and early morning on January 6. By the time the slug reached Seymore, the cyanide concentration had been reduced to .015 mg/1, well within the upper limit of .020 mg/1 specified in drinking water standards.
>
> In addition to the impact of materials on surface waters, concentrations of cyanide were also found in groundwater in the immediate vicinity of the accident. Recovery wells coupled with the calcium hypochlorite treatments were employed until May 23, when the operation was declared completed.

The report* from which the foregoing example was abstracted states "This incident demonstrates that, with a growing population and advanced civilization, the hazards to public health from hazardous chemicals is increasing. All pollution control agencies should and must prepare themselves to handle emergency problems of this nature." *That is what contingency planning is all about: preparing our agencies or* companies *to handle* emergency *problems.*

A Brief History of the National Contingency Plan

As stated above, a contingency plan called the National Multi-agency Oil and Hazardous Materials Pollution Contingency Plan, was prepared by five Federal agencies at the direction of the President. This was essentially an interagency agreement among the Departments of Interior; Transportation; Defense; and Health, Education and Welfare; and the Office of Emergency Preparedness. Each of the agencies, through statute, executive order or Presidential directive, was assigned primary roles because of its resources or expertise that would be particularly useful in cleanup and countermeasure actions.

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*Information extracted and quoted from "Cyanide Pollution and Emergency Duty, Train Wreck, Dunreith, Indiana, January 1968." Indiana State Board of Health.

The Federal Government's efforts to deal with spills of hazardous substances were placed on a statutory base with the President signing on April 3, 1970, the Water Quality Improvement Act of 1970. This new act included, in Section 12, important provisions for coping with spills of hazardous substances and directed, in Section 11, that within 60 days after the effective date of the act there should be published a *National Contingency Plan* to provide for efficient, coordinated and effective action to minimize damage from spills.

Section 12, mentioned above, included a requirement that the discharger of a hazardous substance should immediately notify the appropriate agency of the United States in order to facilitate removal of the discharged material; authorization for the Federal Government to act to remove a hazardous substance discharged to the navigable waters of the U.S. when removal actions are not immediately undertaken by the discharger; and authority to utilize the cleanup fund provided for by Section 11 to effect such removal by the Federal Government.

Pursuant to the provisions of Section 11, the Council on Environmental Quality published on June 3, 1970, a National Oil and Hazardous Materials Pollution Contingency Plan. This Plan was essentially the same as the 1968 Plan mentioned previously because assignments of responsibility for carrying out the new act and regulations implementing its specific elements had not yet been issued. The same five agencies also were still involved.

Regulations required to fully implement the new act coupled with Reorganization Plans Nos. 3 and 4, 1970, (establishment of EPA and NOAA, respectively) made it imperative that the National Plan be again revised. Accordingly, in August, 1971, the Plan under which we are presently operating was issued.

National Contingency Plan—1971

The reorganizations mentioned above caused a restructuring of the response organization. Specifically, there are now eight Federal agencies involved, four Primary and four Advisory. The Primary Agencies are: Environmental Protection Agency, Department of Transportation, Department of Defense and Department of the Interior. The Advisory Agencies, the Departments of Commerce; Treasury; Health, Education and Welfare; and the Office of Emergency Preparedness, are those departments or agencies that could have significant inputs during specific pollution spills, for example, in a spill in the international boundary waters, the State Department would be deeply involved.

The National Plan establishes a planning and response organization called the National Response Team (NRT) which includes representatives of the Primary Agencies and representatives from the Advisory Agencies, as appropriate. The NRT has two major functions; these are: (1) it serves as the national body for preparedness and preplanning before a pollution spill occurs, and (2) it acts as an emergency response team to be activated when a spill: "(a) exceeds the response capability of the region in which it occurs, (b) involves National security or, (c) presents a major hazard to substantial numbers of persons or nationally significant amounts of property."*

Each region has its Regional Response Team (RRT) with functions comparable to those of the NRT, but at the regional level. Federal response activities at the site of a spill are under coordination and direction of the On-Scene Coordinator (OSC), whose duties are specified in the National Contingency Plan.* The OSC is the single executive agent, predesignated by regional plans, to coordinate and direct the Federal pollution control activities. The OSC must be a Federal officer or employee and must be predesignated in appropriate regional plans if Federal resources are to be employed. The Plan establishes that the Environmental Protection Agency shall furnish or provide for the OSC's for all inland navigable waters; the U.S. Coast Guard shall furnish or provide for the OSC's for the high seas, coastal and contiguous zone waters and for Great Lakes coastal waters, ports and harbors. It is interesting to note that, without regard to the Agency supplying the OSC, any environmental pollution control activities must receive the concurrence of the NRT.

The National Plan contains general information on response actions and separates the response into five relatively distinct classes or phases; these are:

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*Sec. 303.3, National Oil and Hazardous Substances Pollution Contingency Plan, August 1971.

*Sec. 504, National Oil and Hazardous Substances Pollution Contingency Plan, August 1971.

Phase I—Discovery and Notification

Reports of spills may be the result of deliberate discovery, through the actions of a discharger or by random, incidental observations by private citizens or others. As mentioned earlier, Federal law requires that any person in charge of a vessel or of an onshore facility shall, as soon as he has knowledge of any discharge that violates Federal law or regulation, immediately notify the appropriate agency of the United States Government of such discharge.

Phase II—Containment and Countermeasures

These are actions to be initiated as soon as the existence of a spill is known. Common sense actions, like closing valves and activating pumps, would be first order countermeasures. Deployment of containment booms to trap material floating on water, buttressing dikes to prevent escape of liquid from a storage agea to a water course and notification of users of the affected waters are also included under this phase. With specific reference to hazardous substances that could not be removed from the water environment, the addition of a neutralizer as in the example cited earlier would be considered to be a countermeasure if accomplished within several hours of the spill's occurrence.

Phase III—Cleanup and Disposal

This includes physical removal of the contaminant from the water environment; safe, noncontaminating disposal of any collected polluting material; and *in situ* neutralization of the effects of the pollutant. The addition of HTH to the waters of East Fork, White River in the Dunreith episode would be classed as a cleanup/restoration action because of the elapsed time factor.

Phase IV—Restoration

This means actions taken to return the water environment to its pre-spill conditions. Some of the kinds of actions that might be taken under this phase are reseeding shellfish beds decimated by a spill, restocking finfish in the affected water body, removal and replacement of contaminated beach sand, or filtering contaminated water through material that removes the pollutant.

Phase V—Recovery of Damages and Enforcement

This can include a variety of activities, depending upon the location of and the circumstances surrounding a particular spill. Enforcement activities under appropriate Federal authority such as the Refuse Act of 1899, the Federal Water Pollution Control Act, as amended, and under appropriate State statutes and local ordinances are included. Recovery of damages done to Federal, State or local property is included; recovery of third party damages, however, is not dealt with in the National Contingency Plan.

Inasmuch as a fundamental precept of most Federal emergency plans is that of committing Federal resources when needed to assist State and local forces, it is important that Federal and State contingency plans be interrelated. To achieve this goal, regional contingency plans developed under authority of the statute and the National Contingency Plan are structured so as to include subregional plans. Development of subregional plans is generally based on State boundaries, and in the inland water areas, most subregional plans have been or are being developed cooperatively by Federal and State agencies.

Guidance for developing regional, State and local contingency plans stems from both the National Contingency Plan and "Criteria for State, Local and Regional Oil Removal Contingency Plans," Title 40 CFR, Part 109, dated July 24, 1971. These criteria were developed pursuant to the provisions of the Federal Water Pollution Control Act, as amended.

This concludes a brief summary of the present National Oil and Hazardous Substances Pollution Contingency Plan; the following discussion is to give you some idea of what we foresee for both the near future and over a longer period.

For the immediate future, development and issuance of new regulations will provide, as in the past, the basis for strengthening the National Contingency Plan. Specific regulations in various stages of development are:

1. Designation of hazardous substances which, when discharged in any quantity into or upon the navigable waters of the U.S., present an imminent and substantial threat to the public health or welfare;
2. Recommended means or methods for removal of hazardous substances; and
3. Revisions to existing regulations covering the administration of the revolving fund.

Over the longer range, as the public's concern for protecting the environment from insults by spills of hazardous substances, we can speculate that the President and the Congress may well decide that hazardous substances discharges will be subject to proscriptions, requirements and penalties comparable to those already provided for discharges of oil. Should such changes in the law come about, it will be necessary to insure that the National Contingency Plan be revised to address hazardous substances discharges more definitively than it does at present.

This has been a brief discussion of the National Contingency Plan, its history and some of its important provisions. This Plan or any other plan cannot or should not be expected to take the place of top quality design and construction of facilities, adequate training of operating personnel, and liberal applications of good operating practices. What a contingency plan can and should be designed to do is insure that resources are identified and the operating mechanism is available to move into action when a spill threatens or occurs. The name of the game is: Preparation!

A STATE CONTINGENCY PLAN FOR HAZARDOUS SPILLS

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INTRODUCTION

Spills of hazardous materials represent an increasingly significant water quality management problem. Water quality management policies in Pennsylvania's water pollution control legislation and in Federal legislation recognize the need for the abatement of all sources of water pollution. In the past most State and Federal regulatory efforts have been oriented toward the clean-up of pollution from existing waste discharges. Recently, however, the Pennsylvania program and programs in other states have been placing increased emphasis on the prevention of pollution.

Some waterways have been polluted to the extent that the effects of spills have been masked by the pollution from the daily discharges of wastes from municipalities, industries and mining operations. As the pollution from "chronic" sources is abated and treatment facilities installed, new uses are made of waters. Aquatic life returns to areas that did not previously support it. Recreational use of waters increases and the "acute" discharges (that is, those from spills or unusual incidents) become a more serious pollution problem. While spills of materials that affect water uses have always constituted a significant problem, as water uses have increased in urbanized areas, the pollutional effects of spills take on added significance. Prevention of and reaction to spills as a major part of water quality management is constantly taking on added importance.

Historically, our state water pollution agency response to a spill has been similar to the action taken by some highway officials when poor road conditions develop and funds or time are not available to make needed corrections or repairs. Under such circumstances highway officials sometimes erect a sign at the entrance to the problem area that warns "Rough Pavement Ahead". This sign warns the motorist to slow down because there is a problem on the road. It doesn't solve the problem but it does attempt to minimize damages to the motorist.

Our state water pollution control agency's response to most spills has paralleled this type of highway department response to poor road conditions. We do not actually erect a sign saying "there has been a spill" but we do warn water users of potential problems and ask them not to use the water. This action can prevent pollution problems for a public water supply or industrial water supply if the warning comes early enough, but does not help the aquatic organisms that inhabit the waters or protect shorelines, boats or in-stream structures just as the highway sign doesn't take the bumps out of the road.

Of course the state action goes beyond warning downstream users of the danger of spills. Every effort is made to trace the source of the spill if it is not known, to order the responsible party to clean-up or neutralize the material, to assess penalties for damages and to make sure that corrective action is taken to prevent a recurrence. Too often these actions do not prevent extensive damages to waters and their uses.

Our state and neighboring states such as New York, Delaware and Ohio operate in essentially the same manner in response to spills or similar pollution incidents.

Spill Prevention

The most important element, in my opinion, in contingency planning for spills should be an effective spill prevention program. For the last few years we have been implementing a pollution incident prevention program aimed primarily at requiring municipalities and industries that have had spills in the past or represent a significant spill potential to prepare and implement a positive plan to prevent pollution incidents. A plan must be developed and implemented that prevents pollution from activities such as transportation, storage and processing of materials (with special emphasis on liquids), and from the breakdown of treatment plant equipment. It requires personnel training in pollution prevention and response to emergencies and requires contingency planning for events such as power failures, floods, strikes and vandalism.

In 1969, Pennsylvania's water pollution control legislation was amended to specifically include the concept of pollution prevention as well as pollution abatement as a major program responsibility. Since that time we have been stressing the development of regulations to control what we consider to be the most serious sources of pollution incidents. One of the first regulations that was implemented attacked the problem of unregulated storage of pollutional material in earthen impoundments with no apparent surface water discharge. In the past we have had a number of serious pollution incidents caused by failure or intentional breaching of impoundment walls. In addition, the contents of these impoundments usually leaked or leached to the ground water causing pollution problems. Regulations now require permits for use of earthen impoundments and include requirements for structural stability, imperviousness, adequate freeboard and protection from vandalism. We believe that this effort will result in a significant decrease in pollution incidents from waste impoundments.

Spill Sources

Spills or pollution incidents vary in size and seriousness from relatively small incidents such as those caused by a farmer washing out his spray equipment or spilling spray materials into a small stream to millions of gallons of waste material being discharged from a broken pipeline, impoundment or similar source. Most spills result from operating problems at industrial plants, pipeline leaks, railroad and traffic accidents and problems at municipal and industrial waste treatment plants.

Most pollution incidents that gain widespread attention are those that affect surface waters. We have experienced a number of spills and leakages to ground water that have created serious pollution problems. Spill response capabilities need to be flexible enough to handle problems with both surface and ground waters.

Communications

In most instances, the notification to our agency of a spill is slower than we would like it to be. It is usually hours after an incident occurs that our agency is notified of a spill. We are attempting to streamline notification procedures since this is an extremely important factor in effective response to a spill. Department regulations and waste discharge permits require immediate notification of any spills or unusual conditions.

Education and possibly imposition of fines can help reduce notification time. We have made arrangements with the Pennsylvania State Police to notify our staff as soon as possible of accidents involving materials that may constitute a pollution hazard. We also have a spill notification arrangement with the Pennsylvania Hazardous Substances Transportation Board. Agreements with state, interstate and federal agencies provide for alerting us of spills in other states that may affect our state's waters.

Communications are an extremely important part of a pollution incident response effort. There needs to be effective communication among various agencies and levels of government involved in spill investigations and clean-up to prevent interagency misunderstandings. Effective communications are needed between an operations center and the field to make sure that the support that is needed in the field is obtained and also that information on conditions can be provided up to the minute. Effective communications are needed to keep press and the public informed as to what is happening.

We have found that keeping the public informed about pollution incidents not only provides information to the public but prevents many problems of false information and concern that need not be created.

Investigation of Spills

Notification of spills usually comes directly to one of our seven regional offices. An investigator from our Department or the Pennsylvania Fish Commission is dispatched to the scene of the incident. Because of the size of the state and the time required for travel to distant parts of regions, a Fish Commission waterways patrolman is often able to get to the problem area earlier than our agency's field investigators. If the available information on the spill indicates that there is or may be a hazard to downstream water users in our state or in other states, the water users and downstream state agencies are immediately notified and contact with them is maintained until the hazard ends. Other agencies such as interstate commissions and the Environmental Protection Agency are also notified of the spill.

Spill Containment and Clean-up

The field investigator has the responsibility of evaluating the conditions at the scene of the spill to determine the action to be taken. He calls for assistance if the situation indicates the need. If he arrives at the scene of an accident where there is a potential for material to cause a problem but the material has not yet drained or been washed into the waterway, he makes every possible effort to insure that the material is contained and cleaned up and disposed of properly. In the case of a railroad or truck accident, the clean-up and disposal is usually done by the transport agency or the company whose product is being transported. In the case of a spill at an industrial installation, the industry has the responsibility of containment and clean-up.

In a case where the effects of a spill are obvious; that is a fish kill has occurred or material is visible in the receiving waters and the source of the spill is not known, the field investigator has the job of tracking down the source of the spill so that the discharge from the source is stopped, that the responsible person is ordered to clean up the spill, that responsibility for damages can be assessed after the pollution incident is ended and that steps can be taken to prevent future spills.

Where spilled material has already entered the stream, the field investigator or investigating team has the responsibility of taking samples and providing information on the quantities of material involved to a spill investigation coordinator in the regional office. The hazards associated with the spill are determined and the water users are provided with this information. If chemical treatment of the stream is needed or materials can be physically removed, the responsible party is ordered to take the necessary action.

From this description it should be apparent that the clean-up and abatement of the pollutional affects of spilled material has been the responsibility of those who have caused the problem. Where the sources are easily defined and the responsible party is cooperative, this system works fairly well. We are concerned that in cases where the responsibility is not clear or the responsible party is not cooperative, little or nothing can be done to ameliorate the damages from the spilled material. Our agency and other states that I have contacted do not have readily available personnel and funds to clean up a pollution problem in such a situation in the time frame in which it should be done. There is a positve effort being made to enhance our state capabilities in this area and this effort will be described later.

Industrial Clean-up Efforts

We have found recently that those persons who are handling, storing or transporting oil and hazardous materials have recognized the pollution problems associated with spills and are better equipped to handle spills than in the past. Many companies, especially oil companies, have special equipment available individually or have joined together in local areas in a consortium to make equipment available to handle problems caused by spilled materials. As an illustration, a group called TRIAD (Three Rivers Improvement and Development Corporation) whose membership includes a number of industries, provides facilities for the clean-up of spills as well as being a group that is concerned with improving the three rivers, the Ohio, Monongahela and Allegheny in the Pittsburgh Area. Groups of oil companies in the Philadelphia area have joined together to make equipment available for spill clean-up. With rapid notification of spills, competent investigation by regulatory people and the cooperation of those responsible for a spill in the clean-up and other corrective actions, spill damages can be minimized.

Unfortunately not all spills come from sources which are easily defined or are caused by people or companies that will take quick action to ameliorate damages. The need for improved state response to pollution hazards from spills was demonstrated in a situation that occurred in our state in the late summer of 1969.

State Response to the Breakout of Polluted Water From an Abandoned Mine

The West Branch of the Susquehanna River Basin is located in Central Pennsylvania and drains 6,955 square miles of the state. It joins the North Branch of the Susquehanna River at Sunbury to form the Susquehanna River.

The West Branch of the Susquehanna River is approximately 240 miles long and drains an area in the upper basin that has been extensively mined for bituminous coal. As a result of regulatory efforts and completion of mining in some areas, quality conditions in the headwaters area which were previously acid, had improved to the point that the river was alkaline and supported aquatic life in portions of its first 35 miles. Most of the next 140 miles of the river are quite acid due to acid drainage from abandoned mine discharges but do improve near the end of the reach. Due to the influence of alkaline tributaries, the final 65 miles of the West Branch of the Susquehanna River (from Lock Haven to Sunbury) are normally of relatively good quality but subject to pollutional slugs of acid.

In late summer of 1969, a coal mine located in the headwaters of the West Branch of the Susquehanna

River that had been dewatered and mined and was then abandoned, began to fill with ground water. The ground water that came in contact with the minedout area became contaminated with acid and iron. When the water in the mine reached an elevation from which a surface discharge was possible, the contaminated waters flowed into the headwaters of the West Branch of the Susquehanna and downstream to a large impoundment that was of relatively good quality and turned the impoundment acid.

Although there are enough acid tributaries to turn the stream quite acid a few miles below the impoundment, the alkaline water released from the reservoir had a neutralizing effect on the stream and provided some protection to areas further downstream where the alkalinity is gradually restored by tributaries. The acid from the mine water breakout that turned the impoundment acid posed a serious threat to the quality of the lower 65 miles of the river and threatened damage to water users and aquatic life in that area and in the main stem of the Susquehanna River.

The seriousness of the situation was recognized and in an unprecedented move the Governor's Office directed that all possible steps be taken to prevent a problem in the lower portion of the river and directed that all state agencies cooperate in this effort. In the initial phases of the response effort, lime was added by the truckload to the West Branch of the Susquehanna River at downstream bridges and other points of access. In the meantime, arrangements were made to obtain large quantities of alkaline materials to be added to the waters being released from the reservoir. Samples were collected throughout the stream length to determine if the neutralizing materials were effectively being used and to determine the trends in the water quality.

A massive neutralization program was established in which sodium hydroxide was added at the reservoir outflow and to the stream above the reservoir. This chemical addition was carried out for a number of months until ground water levels were controlled by pumping and the problem of acid contamination of the reservoir was ended. Waters from the mine are now pumped to a treatment plant and then to another watershed.

To give you an idea of the magnitude to the stream treatment effort carried out from August to February, approximately 1.25 million gallons of 50% sodium hydroxide solution, 4,800 tons of soda ash and 2,600 tons of hydrated lime were added to the stream.

The treatment of the stream and management of water quality on a real time basis was a significant intergovernmental agency effort for our state. It indicated that with special arrangements and cooperation, there was a tremendous capability in state government to handle pollution incidents.

Seven state agencies, four federal agencies, two universities, two municipalities, two water companies and two industries cooperated in the response effort by providing men, equipment and laboratories to operate the stream treatment system. The state agencies involved were the Department of Health, Mines and Mineral Industries, Forests and Waters, Transportation, Agriculture, and the Fish and Game Commissions. The federal agencies participating were the Corps of Engineers, U.S. Geologic Survey, Weather Bureau and the Federal Water Quality Administration. Laboratory facilities were made available at the Clearfield Sewage Treatment Plant, Williamsport Sewage Treatment Plant, White Deer Mountain Water Company, Danville Water Company, Pennsylvania Power and Light Company, and Hammermill Paper Company. Graduate students from Penn State University and the University of Pittsburgh assisted with field and laboratory work.

Because this program had to be continued for a number of months, some very serious personnel shortages were created for other parts of our water pollution control program. However, the benefits of protecting the Susquehanna River from acid pollution were significant. The question as to the financial liability of the mining company that had abandoned the mine, for the neutralization costs, is now being resolved in the Courts.

Our experience on the West Branch of the Susquehanna River indicated that state agencies in cooperation with federal and local agencies and individuals can, if they have the support of the bureaucracy and the leaders in the state government, pull resources together to do an effective job of cleaning up spilled materials or mitigating the effects of a hazardous substance. Because it was a very special and very serious incident that pulled these forces together, we do not expect to routinely be able to pull together such a response without more formal arrangements.

An Improved Response Program

The problem of improving state agency response to spills on a more routine basis was presented to Pennsylvania's Water Resources Coordinating Committee. The Coordinating Committee has appointed a Task Force to develop a pollution incident response capability that can take best advantage of state capabilities for an improved pollution incident response effort.

I am Chairing this Task Force which is developing the framework for an improved state contingency plan. Many of the facets of the plan being developed closely parallel the contingency plans that have been published by others.

Our plan, at the present time, calls for the establishment of an operations center in Harrisburg with a 24-hour a day, seven days a week spill response capability. A specially trained team would be established to serve as a spill response team. This team will include a person who will be the "on-scene director" of field operations in investigating and clean up of spills. This response team would be available for special survey work when not handling spills and other pollution incidents.

The operations center will be the notification point for spills. It will call in the spill response team when necessary and will handle all notification of agencies and see that all water users are notified of possible hazards.

The spill response team will be responsible for having necessary containment measures effected, for initiating measures to abate problems and for generally directing clean up activities of responsible parties. The team will direct the actual clean-up if conditions warrant.

We have found that certain agencies such as the Chemical Transportation Emergency Center (better known as CHEMTREC) are doing an excellent job of providing information on the handling of hazardous materials and we believe there is a significant need for training of our field people and the response team in handling and the dangers of the hazardous substances.

The plan will also include an enforcement and damage recovery program to insure that those responsible for damages are assessed with the costs of abatement and clean-up.

There are a number of problems to be worked out before the response team and operations center concept becomes a reality. One probem that is currently being worked on is that of making the facilities of various state agencies more readily available in case of a pollution incident, and establishing procedures for financial reimbursement for services rendered.

I believe that the most efficient method of neutralizing the effects of the spill is to have the person responsible take the necessary corrective action expeditiously. This procedure places the responsibility where it belongs. However, when events occur in which the source of the problem is not clearly defined or the time it takes to make this determination may be such that, unless the state or federal or local governmental agencies can act, a serious problem will go unresolved and significant damages will result, a governmental agency should be capable of spill clean-up. It is because of this need that we are attempting to improve our response in the area of spill clean-up.

The inability to get approval to make commitments for expenditures rapidly is a major deterrent to an effective spill clean-up program by our state agency. It appears that the only feasible way to have clean-up and containment equipment and facilities available is by hiring contractors on a stand-by basis with prior approved rates for service. Because of this spending constraint, our major emphasis for the immediate future will be placed on developing improved funding procedures while using all available facilities from state, local or private sources to neutralize the effects of hazardous materials spills where it is in the state's interest.

Early warning and notification can be one of the most important factors in effective pollution preventive action. I believe that notification procedures need to, can be, and are easiest to improve. We will probably establish a central telephone number that can be called collect 24 hours a day to report spills to simplify spill reporting on a statewide basis and then advertise widely that this number should be called.

CONCLUSIONS

In most instances, pollution incident response in our state and in others surrounding Pennsylvania needs to be improved.

Prompt notification of spills is necessary so that downstream water users can be warned of hazards, steps can be taken to keep as much material as possible out of the waters and corrective and clean-up actions can be initiated.

Most clean-up activities are carried out by those responsible for a spill. Current staffing and funding procedures make it almost impossible for our agency to react quickly to clean-up a spill where there is no responsible party available or willing to undertake the clean-up. We are working to improve this situation by developing a state contingency plan utilizing as many agencies in state government as possible as participants. We need to overcome staffing and funding problems to develop a more workable plan and implement it.

As chronic pollution sources are cleaned up, the need for a program to prevent and react to spills is taking on added significance as an important facet of a water quality management program. We are hoping to be able to not only minimize the number of spills that occur but to also react quickly when one does occur and do more than put up a sign that says "There has been a spill."

A LOCAL CONTINGENCY PLAN FOR HAZARDOUS MATERIAL SPILLS

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INTRODUCTION

That crescent shaped slice of the lower Texas coastline opposite the hub city of Corpus Christi is better known as the Coastal Bend area. The area serves nearly 250,000 people in five municipalities, all on the shores of an interconnected fifty-mile stretch of shallow water. These waters are protected from the Gulf by a chain of islands extending up from Brownsville to near Houston. (See Figure 1).

A subtropical climate is enjoyed by the residents of the area and by a thirty-five million dollar per year tourist trade. The shallow, temperate waters productively serve the commercial fishermen and also provide a vital nursery for Gulf of Mexico marine life. Preservation of the area as a marine life nursery is urged by all users of the waters for whatever reasons.

A deep water channel from the Gulf through the island chain at Aransas Pass serves the City of Corpus Christi and is the reason for this City being the ninth largest port in the U.S., serving four major oil refineries, a number of petroleum pipeline terminals, and many other industries requiring shipping facilities. The Coastal Bend waters border other major petroleum storage and shipping facilities, harbor over six hundred producing oil and gas wells, and serve as a highway for transporting over 250 million barrels of petroleum products per year. Development of the underlying minerals continues with relatively small activity compared to that of prior years.

Obviously, the Coastal Bend waters are highly exposed to petroleum spills of all types and up to major dimensions. It has not experienced the type of spill that could be classified as major or catastrophic, yet the area is certainly not without its frequent nuisance-type spills. A unique community pride and happy coexistence combined with a deep concern for protecting the environment, the ecology, and the aesthetics of the Bays prevails throughout the Coastal Bend area, and this attitude may in part be the reason that the area has avoided a major spill through a "try harder" attitude. This attitude is undoubtedly the reason why the area took early steps to prepare in some manner to contain and clean up a massive petroleum spill.

History

The Santa Barbara incident in early 1969 alerted the remaining coastline of the U. S. that it, too, was without the equipment or expertise to contain and harvest a major petroleum spill. We soon learned that the Santa Barbara harbor had suddenly become a laboratory of sorts for all types of experiments utilizing chemicals and sorbent-type materials which generally proved ineffective, adding to the already debris laden waters and making the cleanup job in the harbor area that much more difficult. Confusion and waste motion was obviously created in part by so-called overnight self-made experts fanned by conflicting statements from the uninformed and the misinformed. Certainly we all learned something from the Santa Barbara incident, even though that be what not to do.

The Coastal Bend area quickly decided to profit from Santa Barbara's mistake and agreed to take some action. On August 28, 1969, ten major oil companies, five major refiners, three Federal agencies, four State of Texas agencies, three coastal County governments, four municipal governments, and a good representation from the public at large, met in Corpus Christi at the request of that City govern-

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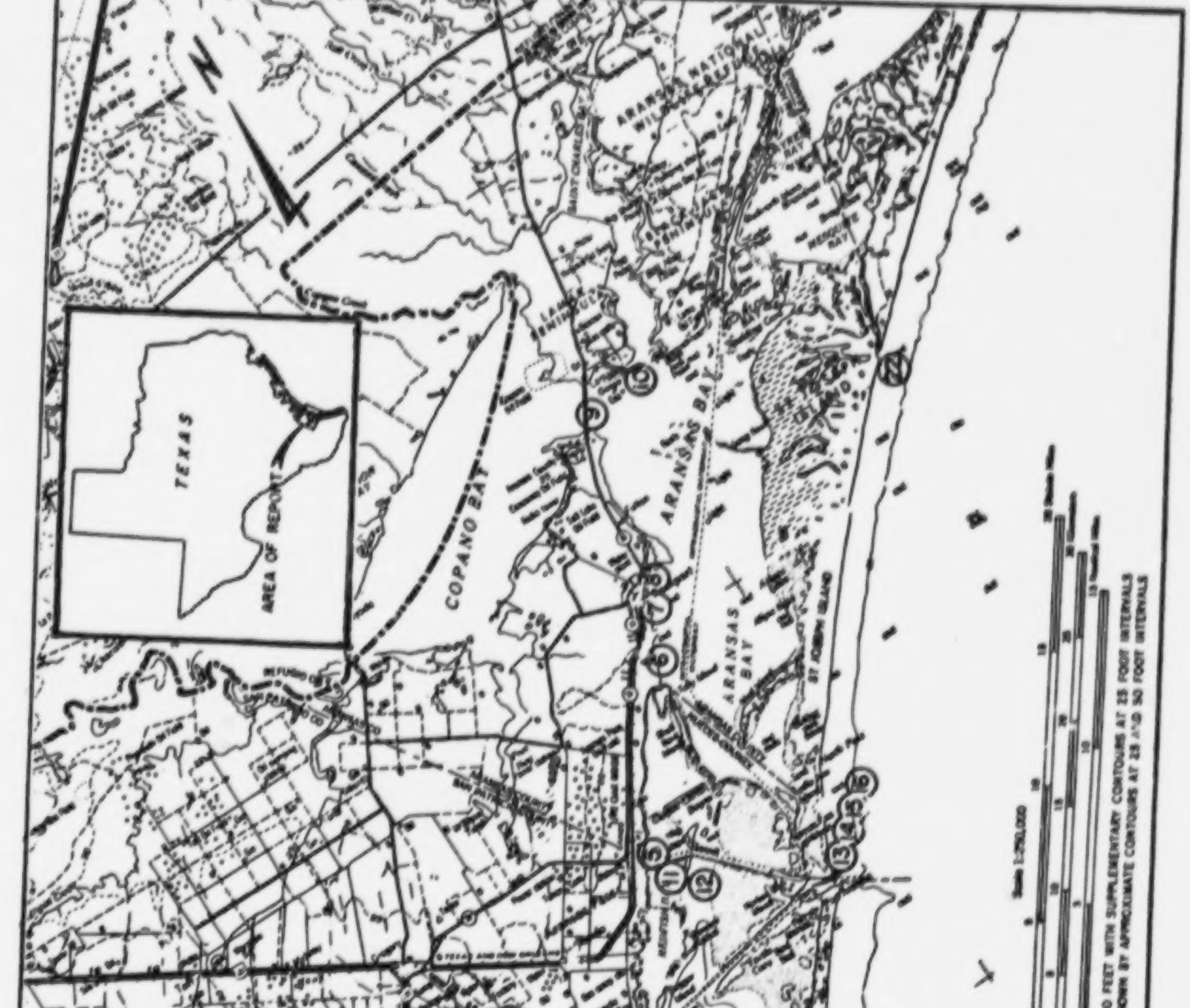
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TEXAS
AREA OF REPORT
COPANO BAY
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NUECES BAY
CORPUS CHRISTI
ST JOSEPH ISLAND
POSSIBLE CLOSINGS CONSIDERED
CONTOUR INTERVAL 50 FEET WITH SUPPLEMENTARY CONTOURS AT 25 FOOT INTERVALS
RELIEF PARTIALLY SHOWN BY APPROXIMATE CONTOURS AT 25 AND 50 FOOT INTERVALS

Figure 1: Coastal Bend Area

ment, to ponder the problem. This group soon agreed to the need for a comprehensive study concerning the waters and exposure of the area, for the purpose of deciding what action should be taken to reasonably prepare the area against a very possible massive petroleum spill. To accomplish this undertaking, a representative fourteen-man Steering Committee was selected to oversee the overall project. A five-man Legal Committee was appointed, selecting a member from each of the Federal, State, and local governments. The fourth legal member came from industry and the fifth member, acting as Chairman, represented the public at large. The group then contributed a five-man Working Committee to make the study, and the complement of this Committee was: W. A. Sky-Eagle, Jr., Area Engineer, U. S. Corps of Engineers, representing the Federal agencies and acting as Vice Chairman of the Committee; T. G. Post, District Director, Railroad Commission of Texas, Oil and Gas Division, representing the State agencies; Delmer E. Snow, Vice President and General Manager, Refinery Terminal Fire Company, representing the five refiners of our area; Neal G. Turner, District Production Supervisor, Atlantic Richfield Company, representing the oil and gas companies operating in these waters; and I, Petroleum Superintendent for the City of Corpus Christi, representing the local governments and acting as Chairman of the Committee. Contributions in the amount of $20,000 were received to defray the expenses connected with making the study.

The Working Committee was charged with the following:

1. Determine what water bodies in the coastal portion of the three counties can and should be closed off in the event a major petroleum spill should occur outside these waters. What equipment would be required to accomplish this and what would be the cost?
2. What equipment would be required to contain a major oil spill in the larger water bodies of the area and what methods should be employed to harvest the spill? What would be the cost of this equipment?
3. Prepare a contingency plan for the three county area.

Scope

On May 28, 1970, after nine months of intensive and full time study, the Working Committee submitted its report, findings, and recommendations to the fourteen-member Steering Committee. The Steering Committee approved the report and recommendations and, in turn, recommended their adoption and implementation by the community at large.

During the nine months study period, the Working Committee, after thoroughly investigating the bodies of water and oil spill problems of the area, visited some fourteen port cities along the West, East, and Gulf coasts. At each port, the Committee conferred with Federal, State, and local regulatory agencies having any connection with oil spills and, also, with those in private industry that might be responsible for such spills. The Committee conferred with all those private contractors whose services had previously been employed to contain or remove an oil spill. During the study period the Committee attended all major conferences concerning containment and removal of an oil spill and, also, investigated studies already underway for the development of new equipment or techniques. We continue to keep abreast with new equipment and techniques.

On November 13, 1970, the authorizing group initiating the study at that meeting held August 28, 1969, received, approved, and adopted the Steering Committee's recommendations, as well as the Legal Committee's recommendation that a nonprofit corporation be established to implement the recommendations.

The approved recommendations covered the following principal items:

1. Purchase and selectively store $206,000 worth of equipment and material.
2. Implement a contingency plan adapted to the needs and environment of the Coastal Bend waters.
3. Establish the Corpus Christi Area Oil Spill Control Association, a nonprofit corporation, as the vehicle to control the equipment and develop the expertise in its use and, also, to implement the contingency plan.

Major purchases of equipment and material include 8,500 feet of three different types of container boom, 20,000 bales of straw, one 40-foot marine craft, erection of two metal quonset type warehouses, construction of a portable marine skimmer designed by the Working Committee, and a number of other such items as hay blowers, chemicals, mixers and sprayers, floating saucer-type skimmers, a communications system, anchors and cables, and other minor items such as hand tools and the like.

All of the equipment or material recommended for purchase and storage was selected on the basis of portability so as to permit quick response to a call for containment or removal of an oil spill. The selection was also influenced by a criteria that the equipment or material be operational in our shallow waters under slightly above normal climatic conditions. In the Coastal Bend area this means wind velocities in the 20 to 25 mph range and waves 1-1/2 to 2-1/2 feet high.

Contingency Plan

The oil spill contingency plan adopted by the Coastal Bend area is a plan of action. It is not a tried and proved handbook to prevent damage from oil spills. Many variables limit the ability of man and his equipment when using it to react to the forces of nature. The plan is, however, a tool put in the hands of those in the Coastal Bend area to use in emergency situations so as to alleviate, if possible, costly damage to property and/or environment.

Implementation of the contingency plan is through the Corpus Christi Area Oil Spill Control Association, a nonprofit Texas Corporation chartered in December of 1970. The Association is governed by a five-man Board of Directors representing the Federal government, State of Texas, Coastal Bend area Navigation Districts, industry, and the fifth member representing local municipal and county governments. The Board is charged with establishing the means and wherewithal to effect the purchase of the required equipment and implement the plan itself.

The operative side of the Association is run by a Manager and Superintendent who, with a secretary, comprise the entire permanent staff. The Manager is responsible to the Board and is charged with programming, budget matters, selection of the prime contractor for each area, authorizing containment and cleanup expenses, keeping abreast with new equipment and techniques, coordinating between various government agencies and membership and, most important, keeping the community informed on the subject of oil spill containment and its removal. The Superintendent is responsible to the manager and is charged with proper storage and maintenance of equipment owned by the Association. He is to develop the expertise in use of the equipment through the "fire drill" training of personnel from the prime contractor. The Superintendant is charged with maintaining a current inventory of other available equipment and labor force. He will keep abreast with new equipment and techniques as well as frequency of spills in the area and how they were contained and/or removed. In other words, the Superintendent is charged with maintaining expertise and readiness.

Although the plan has been developed to provide capability in combatting large petroleum spills, it may be activated in whole or in part to clean up small spills. It will be activated at the discretion of the Plan Manager, under the following circumstances:

1. When requested by the responsible party.
2. When requested by a responsible governmental agency.
3. When the Captain of the Port, with the concurrence of the Plan Manager, declares that the offender's method of cleanup is inadequate and calls upon the Association to take over cleanup operations.
4. When the offender is unknown, the Plan Manager, with the concurrence of the Captain of the Port, is authorized to proceed with initiating containment and removal operations at his discretion when loss of life or property can be prevented by taking immediate action. Limited funds are provided only to give time for possible search for the offender and/or securing other funds from other sources.

Equipment which is owned by the Association and made a part of the plan may be rented by the individual operators or agencies for their own use, at established rental rates. All costs associated with restoring or replacing warehouse equipment so rented from the Association shall be borne by the rentor. The Plan Manager shall decide whether mechanical equipment may be rented without its regular operator.

The fifty-mile stretch of coastal waters covered by the plan is divided into two sections called Area "A" and Area "B". Area "A" being that portion of water lying south of the Aransas Pass-Port Aransas causeway and extending southward to the Nueces-Kleberg County line. Area "B" is that water area extending northward including Aransas Bay and Copano Bay and on to the Aransas-Calhoun County line. A prime contractor has been selected for each area. The Association will have only to deal with the prime contractor of each area who, in urn, will be called upon to marshal all of the other equipment and personnel available by the other contractors in the area. This precludes the necessity of dealing with more than one service contractor at a time and should result in a quicker response. Of course, all of the equipment and material owned by the Association is and will be made available to the prime contractor. A storage warehouse is located at an accessible waterside site in each area.

The contingency plan was designed to service the community at large and not just a segment, either private or government. It dovetails with the State of Texas and national contingency plans, therefore, the entire operation and equipment could be made available to either State or national concepts if and when regional areas and teams are established in the future.

The design of the plan and selection of equipment for use in our shallow waters should not be considered a panacea with regard to all different types of petroleum spills, and under all types of climatic conditions. The entire concept is considered to be operational only under normal and average climatic conditions and dependent to a great degree on a satisfactory communication system. Prompt notice will be imperative to effectively contain and clean up any spill at the source site. Once a spill has occurred and spread over a great area, then the use of the more primitive methods need to be employed, such as use of straw, along with a large labor force to remove the straw and carry it to places for disposal. To assist in early notification, the Association will request cooperation from all agencies, industry, and private individuals, to immediately report all spill incidents. We will, by necessity, have to depend upon notice from other sources, since we will not be in a position to provide continued surveillance over the fifty-mile water area.

The equipment purchased and the plan adopted by the Coastal Bend area is primarily oriented to containment and removal of petroleum spills. It can and will be implemented for containment and removal of any other floating types of chemicals or materials. With development of expertise and use of other equipment, it is possible that the concept might be expanded for other uses within or without the area.

Implementation of the plan at any time will not relieve the responsible party for effecting the containment and/or cleanup. The Association, in implementing the plan, will be acting much like a contractor protected by an indemnity agreement; therefore, responsibility and direction of spill cleanup operations must and will always remain with the party responsible for the spill and employing the services of the Association.

In funding and implementing the contingency plan for the Coastal Bend area of south Texas, no claim is made that this method is the best system or one adaptable to all of the other sections of our U.S. coastline. The area does, however, take pride in demonstrating the results of a community effort to prepare itself against the real possibility and risks connected with a major or massive petroleum spill. Establishing a capability in this area has helped to relieve the important anxiety of a community wishing to prepare itself against possible disastrous spills, and to this end the area can point to the fact that it has done something about the problem.

A CONTINGENCY PLAN FOR RESPONSE TO A CHLORINE SPILL

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INTRODUCTION

As a highly reactive, gaseous element, chlorine is never found in nature in an uncombined state. Thus, unlike the less reactive elements that could be observed and examined by ancient experimenters, chlorine and its properties have been known to science for something less than 800 years.

Chlorine was first produced in essentially pure form by Carl Scheele just two years short of two centuries ago. It has been used industrially for 183 of these years.

To begin with, chlorine was used in a single industrial operation, textile bleaching. Generated from salt, sulfuric acid and manganese dioxide, it was rather expensive to make and somewhat difficult to handle, for its properties were not as well known then as they are today.

The commercialization of two inventions started chlorine on its widescale use.

The first production of chlorine through electrolysis dates back to 1800, and a chemist named William Cruickshank. Chlorine's first liquefaction was achieved by Thomas Northmore six years later in 1806.

Since the early work on electrolysis depended on battery power, it was many years before this production route became practical. Commercial processes would wait for the invention of even more efficient electrical generators by Edison, Siemens, and others. Chlorine and caustic potash were first commercially produced by electrolysis in Griesheim, Germany, in 1890. Chlorine and caustic soda were first made commercially in the United States three years later in Rumford, Maine.

Predating by a few years the commercial production of electrolytic chlorine was the discovery of how to ship it in iron containers, and the answer was simple—keep chlorine free of moisture.

Thus by 1900, both the technology for producing chlorine in large amounts and that for shipping it economically were available, but one further point had to be accounted for before chlorine could take its rightful place as a useful chemical building block. That point, of course, is safety—safety in making chlorine, safety in handling and shipping it, safety in using it.

And I am happy to be able to report that this is a responsibility that chlorine manufacturers have accepted, both as individual firms and, in the years following 1924, as members of the Chlorine Institute.

Today, in part due to these safety efforts, the production, shipment and use of chlorine are all big business. Chlorine productions in the United States last year exceeded 9,300.000 tons.

In order to discuss the safe handling of chlorine, let us divide this production total into two parts—the chlorine that is used in the locations where it was generated, and that used in other locations. As anyone attending a meeting in a chemical center like Houston can realize, much of the chemicals produced in one spot will be consumed in the same area. This is certainly true of chlorine which is produced in four locations in Houston and six more in Texas alone.

The Chlorine Institute estimates that in 1971, about five million tons of chlorine were used in the locations where manufactured. And while safety and emergency procedures are certainly important at such locations, they are directed by and under the control of specially trained safety personnel in a way that the remaining four and one-fourth million tons of chlorine shipped to consumers at non-producing locations is not. The allocation by transportation method is of some interest:

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	Percentage	*1971 Tonnage*
Rail	66%	2,805,000 Tons
Pipeline	17%	723,000 Tons
Barge	13%	553,000 Tons
Ton Containers and Cylinders	3%	127,000 Tons
Tank Trucks	1%	42,000 Tons

Note that the statistics reflect shipments from producing plants; shipments by repackagers would show considerably higher amounts in small containers.

Accidents—General

Along with the other compressed gases shipped in large volume, loss of product due to transportation accidents has been thought of as a *leak* rather than a spill. Liquified compressed gases, of course, can and have spilled out of containers, but their physical properties promptly result in a gas cloud. Should the leak occur on a waterway, the result is of course closely related to the solubility of the material in water. Chlorine happens to be only slightly soluble in water—about 7 pounds per 100 gallons at 60°F (about 1% by weight) so that a large part of any spill still vaporizes. In most flowing streams, dilution and the reaction with the impurities in the water will soon reduce the concentrations to acceptable values.

Because it is not flammable, the primary hazard connection with a large chlorine emission is the formation of a large toxic gas cloud. As any of you who have explored the subject already know, the prediction of gas cloud travel is a difficult business at best. The chairman of one of our committees, Mr. A. E. Howerton, presented a paper on this subject at the March 1969 National meeting of the A.I. Ch.E. Its title is "Estimating the Area Affected by a Chlorine Release." Copies are available from the Chlorine Institute.

It would be dangerous to try to summarize the paper since a thorough and careful reading is called for. It can be pointed out, however, that the cloud travel and spread are very significantly affected by the local weather. One example given in the paper shows a cloud travel of 2 miles with stable conditions and 500 feet with unstable conditions—a ratio of about 20 to 1.

In addition to these difficulties of prediction, the time available for evacuation downwind is always very limited. With only a 5 MPH wind, the cloud will reach a distance of two miles in only 24 minutes.

For these reasons, the industry has traditionally focused its efforts on keeping the chlorine in the container. It has been quite successful in this endeavor—in the 62 years chlorine has been shipped in tank cars, only 5 loads have been lost. Only one death has resulted—a year old infant in a house near the railroad tracks.

Rail Shipments

Given the major emphasis on shipment by rail, let me begin this outline of chlorine emergency procedures with a summary of procedures as they involve rail transportation.

Though chlorine can be shipped by rail in ton containers loaded on TMU cars, the basic method of shipment is in single-unit tank cars. Chlorine has been shipped by tank car for 62 years, ever since the date in Autumn 1909, when the Goldschmidt Detinning Company shipped a specially-constructed 15-ton tank car from Wyandotte, Michigan, to Carteret, New Jersey. The specifications for this car are apparently lost, so we do not know how this car compares to the first standard chlorine tank car, which was proposed in 1912, just two years after the Master Car Builders Association had established its first standard for any type of tank car.

The specifications were quite simple, comprising only three sentences:

> "1. Liquefied chlorine gas may be shipped in a lagged tank car of approved design, which shall be tested before being put into service with a cold-water pressure of 300 pounds per square inch, and stenciled in accordance with the requirement in this respect of the specification for ordinary tank cars.
>
> 2. Car shall be provided with an approved design of small safety valve and fusible seal, which must be so located that in case the car became involved in a fire the seal would be exposed.
>
> 3. The designs for these 'special tank cars' to be submitted to the Master Car Builders Association for approval."

By 1918, these specifications had been extended to become the basic specifications for the American Railway Association's class V tank car, and the commodities for which this class of car could be used extended from liquefied chlorine to such other chemicals as sulfur dioxide, anhydrous ammonia, and propane. The test pressures for the tank went from 300 pounds per square inch to 500 pounds. These 1918 specifications also carried the note:

> "It is so vitally important, because of the character of the commodities to be shipped in these cars, that the tank shall be absolutely tight, that riveted tanks will not be permitted, and all seams shall be welded."

Effective in 1927, the ARA specifications were superseded by those of the ICC, and the ARA V replaced by ICC105A500. In 1941, the new category

ICC105A500W was established to cover cars having fusion-welded, rather than the forged lapwelded steel tanks of the previous specification. It is under this specification, now DOT spec. 105A500W, that chlorine cars are constructed today. Such cars have a tank of a minimum 5/8-inch of high-strength steel, surrounded by 4 inches of thermal insulation and an outer jacket of 1/8-inch steel. These cars have proved themselves in rigorous service.

Today, there are chlorine cars in service with net capacities of 16, 30, 55, 85, and 90 tons.

By industry efforts, coordinated through the Chlorine Institute, every chlorine tank car has an identical arrangement of standardized valves. This standardization program had its origin just two years after the founding of the Chlorine Institute. After a hurricane devastated Florida in 1926, thousands of chlorine cylinders were shipped into the state to get chlorination and sanitation programs back underway. But when the cylinders arrived, it was found that the fittings on many cylinders didn't match those at the water works, for producers had their individual standards, and water works had adopted the arrangements of their own suppliers. Adapters and valves were rushed in, so as to avoid the threat of a typhoid or cholera epidemic.

The need for standards became apparent and the Institute assumed responsibility for setting industry-wide specifications for valves and fittings used on chlorine cylinders. Soon this mission was broadened to include fittings on ton containers and on tank cars.

Over a thousand different valve designs were tested and a single type for each use was agreed to. After industry committees made their selections, the choices were cleared by the Association of American Railroads and the Interstate Commerce Commission, and these new standards were adopted by every chlorine producer.

This standardization has made possible a further safety development—the design and construction of standard emergency kits. Early versions of these kits, which first became available in 1939, contained hoods and clamping devices to control and seal leaks in chlorine containers. They have undergone much continued development.

Since every chlorine tank car has a tank with just one opening, and five valves mounted on its cover in an identical configuration, the control of leaks is far more routine than on tank cars carrying commodities where different valve configurations may be involved.

A Chlorine Institute emergency kit "C" is used to control leaks in a chlorine tank car. There are currently about 700 such kits spotted throughout the United States and Canada. The arrangement of valves on top of a chlorine tank truck is identical to that on the tank car, so the emergency kit "C" can also be used to control leaks here.

While each of the Chlorine Institute emergency kits has a detailed instruction book, the Institute has also begun to prepare supplemental instructions in slide form.

Transfer by Pipeline

Many chlorine pipelines, transporting both gas and liquid, exist today. Some are as long as two miles, and their number and length are constantly increasing. Though transfer by pipeline represents the second-largest method of transport, it, like chlorine consumed at producing locations, is generally under close engineering supervision. Thus pipeline chlorine is somewhat outside the scope of this paper.

Shipping Chlorine by Barge

While some 6900 tank cars were used to transport the 2,800,000 tons of chlorine that the Chlorine Institute estimates were shipped by rail in 1971, it took only 65 chlorine tank barges to transport the 550,000 tons that were shipped by water. Obviously, then, barge capacity is greater than that of rail tank cars. The barges now in use range in capacity from 550 to 1200 tons, divided among as many as six tanks. The use of barges to ship chlorine is a far more recent development than that of tank cars, having begun in 1944. Chlorine barges operate primarily along the Mississippi and its tributaries and along the Gulf Coast. A few are in service from Oregon north to Alaska.

Chlorine tank barges are built to rigorous U.S. Coast Guard specifications, including hydrostatic testing at 450 pounds per square inch. A typical 300-ton barge tank is made from one and one-quarter inch steel, 75 feet long by 11 feet in diameter.

Such conservative specifications have proved worthwhile, since at no point in the past 27 years has a chlorine barge required more than the nominal use of an emergency kit to seal slight leaks in tank valves. You may recall, however, that loaded chlorine barges have sunk near Natchez, Mississippi, in 1961, and near Baton Rouge, Louisiana, in 1965. This second sinking was a result of hurricane Betsy. In neither case did any leakage occur, with the tanks found to be in good shape when they were raised from the bottom of the river, even, in one case, after 18 months exposure.

As a result of these occurrences, the Chlorine Institute set up a task force to investigate the possibility of installing electronic equipment to make it easier to locate sunken barges. The result of this was the development of "pingers," sound transmitters that automatically go into operation when they are submerged in brackish water, or when 10 feet or more deep in any kind of water. When actuated, each "pinger" transmits a special, coded signal for not less than two weeks, so as to give searchers adequate time to locate the submerged barge, no matter how muddy the water in which it has sunk.

The Institute has available for hire three acoustical direction-finders which can home in on the sounds transmitted by the "pingers." These receivers are located in New Martinsville, West Virginia, Calvert City, Kentucky, and Geismar, Louisiana, and are available complete with trained crews, for emergency calls.

"Pingers" have been installed on every chlorine barge. The cost of the hardware for this single safety project, incidentally, was over $135,000.

Ton Containers and Cylinders

Though the quantities of chlorine shipped in these smaller containers are considerably less than the amounts transported in bulk, the safety aspects are quite important, since it is precisely these containers that are used by persons who are likely to know the least about chlorine and its properties.

Thus, emergency kits suitable for sealing the valves and container walls are available. Almost 1500 type B kits are located throughout the United States and Canada. The Chlorine Institute is preparing slide series on how to use these kits.

Accident Handling

Because many accidents, especially railroad derailments, involve several commodities, it is nearly impossible to set forth cook-book style instructions for their control. As a matter of fact, most experienced people would say that you can't really *control* an accident—you just do the best you can with it. These situations put experience at a decided premium and it is for this reason that our industry along with most chemical shippers, feels that the preferable response method is to provide immediate verbal advice and to send experienced personnel to the scene. Although we can all postulate situations which will not wait for this, the actual record shows that it is not a bad technique. In many situations, the inexperienced handling of damaged containers has been the cause of the really serious problems—and very often this can be avoided by waiting for the experienced man to arrive.

Cooperative Control Projects

Because of the realization that any chlorine accident resulting in major damage or personal injuries might result in considerable restrictions on future chlorine shipments, it has always been the informal policy of chlorine producers to send "good samaritan" teams to the scene of any actual or potential chlorine release. Each producer has of course, supplied its own customers with appropriate emergency-call telephone numbers, but teams have willingly gone out to emergency scenes even when their own company's product was not involved at all.

At our annual meeting just over a month ago, the Institute took action to set up a formal chlorine emergency plan, Chlorep for short. The plan will operate in both the United States and Canada; it will use the MCA's Chemtrec in Washington as the dispatch agency in the U.S. and the CCPA's TEAP for dispatching in Canada. One of our committees will be meeting in just a few days to set up primary response areas for chlorine emergency teams and to finalize other details.

Chlorine emergency teams are being set up at most of the chlorine producing plants in the United States and Canada. These teams have responsibility for giving advice and when necessary, going to the scene of any emergency that occurs within their geographic territories. Each team conducts periodic drills with appropriate safety equipment, and has set up procedures for quick transport of personnel and safety devices to an emergency scene. Depending on the type of chlorine shipping container that may be involved in the emergency, they will bring with them Chlorine Institute emergency kits A, B, or C. Procedures will be set up for liaison with local officials before the chlorine emergency team gets to the scene, and with state and federal regulatory officials, trade association, chlorine shipper, and with their own home plant officials once they are at the scene. Hopefully, by setting up this program in advance we may eliminate some unexpected last-minute problems. At one point, for example, a group flying to an emergency was refused passage on a scheduled airline because their baggage included self-contained breathing apparatus—Air Paks—something that a team would always take to an emergency scene. The reason the airline gave was that compressed air cylinders are officially restricted. Having been refused, the emergency team chartered the only small plane available at the airport, only to have its engine fail as it started down the runway. At this point, the team gave up and rented a car for the seven-hour drive to the scene. Thankfully, this did not have the serious consequences it might have had. But the Chlorine Institute has since worked with the Air Transport Association's restricted articles policy advisor group to set up procedures to allow such apparatus to be taken on scheduled airline flights.

Accident Statistics

How often are chlorine leaks encountered? Thankfully, damn seldom. Well over the proverbial 99 and 44/100ths per cent of all such shipments go through in safety. During 1968 and 1969, there were 57 known incidents involving leaks or potential leaks. The Chlorine Institute has received full reports on 48 of these, 27 of which occurred at consumer locations and 14 during rail movements. (The other 7 involved producers, repackagers, distributors, and other forms of transport.)

In 1968 and 1969, some 100,000 tank-car loads of chlorine were moved in the United States and Canada, and it is against that total that those 14 rail incidents must be measured. Twelve of these were derailments, none resulting in a chlorine release. The thirteenth involved a slight leak discovered in a 55-ton tank-car cover plate during yard operations. It was easily repaired.

The other incident was more serious. An empty 16-ton chlorine car was positioned in front of a 16-ton chlorine car on a customer's siding. The empty car was to be picked up by the railroad. The car in use was blue flagged but, due to the empty pick up, the derail was not in proper position. Apparently, when the railroad crew attempted to pick up this particular car, due to the load already in the string, they miscalculated their ability to stop. The empty car was hit with considerable force, driving it into the car being used. This forced the full car off the end of the track approximately 27 feet. This movement of the full car broke the chlorine line, setting the chlorine car's ball-check, excess-flow valve, but allowing the liquid chlorine within the plant line to discharge into the immediate area. None of the personnel outside was affected by the chlorine gas produced, but the gas cloud was moved by the wind through a large door into a work area in a nearby building. Three people were affected by the gas and were taken to the hospital. Two were released immediately, and one was held overnight for observation.

To an industry that has paid as much attention to safety matters as has The Chlorine Industry, any accident involving gas release is regretted. You may be sure the Industry will do its part to minimize the chance that this type of thing might happen again. In this case, the customer was shown the passage from the chlorine manual, a 36-page handling guide published by the Institute, which recommends that a derail be placed at least 50 feet from a tank car whenever it is being unloaded.

As I hope you can appreciate from the points I have outlined, the Chlorine Industry, working through the Chlorine Institute, takes the subject of safety rather seriously. We see no reason to relax our vigilance.

PRESENT AND FUTURE TECHNOLOGY REQUIREMENTS FOR THE CONTAINMENT OF HAZARDOUS MATERIAL SPILLS

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ABSTRACT

From the standpoint of environmental protection, the most effective way to control a spill of a hazardous material is to contain it in its most concentrated form. The advantages of prompt containment of spills in general and acute releases of hazardous materials in particular are (1) minimization of damage to the total environment (2) facilitation of on-site cleanup operations, and (3) prevention of dispersion into watercourses. Almost every spill is a special case by reason of (1) the diversity of hazardous materials, their containers, and the spill situation (during storage or in transit) and (2) the unpredictability of geographic location, time of day, and weather conditions. The problem of controlling hazardous material spills is made more difficult by the lack of extensive experience in spill containment and by the absence of readily available specialized countermeasure equipment near the spill site. Physical barriers for deployment in watercourses, foam diking, and emergency plugging of leaking containers and tanks are three containment techniques now under investigation by Environmental Protection Agency contractors. Requirements, guidelines, and applicabilities for other containment procedures are reviewed and exemplified.

INTRODUCTION

Hazardous material spills are recognized by the U.S. Environmental Protection Agency as a threat to the total environment. Section 12, "Control of Hazardous Polluting Substances", of Public Law 91-224, "The Water Quality Improvement Act of 1970", specifically directs attention to the development of regulations and approaches for controlling and preventing hazardous material discharges into the aquatic environment.

Responsibility for EPA's national research program in this area rests with the Edison Water Quality Research Division of the National Environmental Research Center, Cincinnati. The development of necessary technology and systems for preventing, controlling, monitoring and cleaning up spills of hazardous materials in waterways is the prime function of this Research Division. While the thrust of this paper is on the impact of spills in water, it is recognized that air pollution and ultimate disposal problems generated by such spills are equally paramount. These aspects are broadly covered in this presentation and in greater detail by other authors at this Conference.

Within the context of total environmental protection, the prevention of spills of hazardous materials is the most important line of ecological defense. The danger to the public health and welfare and the insult to the ecology are only infrequently limited to the immediate spill area, even when prompt containment is achieved. Realistically, the damage from a spill cannot be confined exclusively to the water, land or atmospheric ecosystems. Further, in some fortunately rare cases, occurrence of a spill means

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that, in order to preserve the human lives endangered by the spill, damage to the environment must be allowed.

For those directly involved in a hazardous material spill, personal safety is the first consideration, followed by warning and assistance to others. Attention must then be given to halting or containing the spill along with notification of appropriate Federal, State, and local authorities, affected water and sewage treatment plant supervisors, industrial plant managers and safety crews, and cognizant police and fire departments. The very diversity of those who must be alerted points out the totality of the environmental impact of a spill.

Basically, containment is needed to insure environmental protection: the more efficient the containment, the greater the protection of the environment. Spills, as well as chronic discharges, of hazardous materials at significant levels are unnecessary releases that pollute the air, water, and land environment. Such discharges result from accidents, carelessness, bad procedures, poor attitudes, and other practices that are not responsive to the public interest. Technically, this paper is addressed to the problem of the containment (or re-containment) of hazardous materials following a spill or acute release; the case of chronic, long-term, slow release is considered only incidentally. While the need to prevent a spilled material from entering a watercourse is emphasized, the requirements for protecting the atmosphere and earth are given explicit attention.

Importance of Containment

The advantages of prompt containment of spills in general and of crisis discharges of hazardous materials in particular are: (1) minimization of damage to the total environment, (2) facilitation of on-site cleanup operations, and (3) prevention of dispersion into watercourses through flow into sewers, run-off into streams, and percolation into the earth with subsequent seepage into sub-surface water supplies.

The fundamental importance of containing a spill is basically the need to maintain lateral and vertical control of the material. Loss of lateral control implies that spreading will occur. The more spreading, the more widespread the surface damage to the environment and the greater the difficulty of detoxification and clean-up. Vertical spreading, of which percolation and seepage of liquids serve as examples, leads to contamination of well and sub-surface water supplies and makes the process of natural environmental restoration much less rapid because of long term retention and slow release. The spill of a gas or of a volatile material is another example of an accident in which vertical control is lost; as in the case of percolation and seepage of a liquid, lateral control is also eventually lost. Realistically, there are no practical situations in which loss of control is always exclusively vertical or lateral. Spill situations in which there is primarily a loss of vertical control (as in seepage of liquid or venting of gases) are much more difficult to contain. Control, then, generally depends on passive or natural countermeasures for environmental protection or restoration. The rapid dispersion of a spilled gas makes containment impractical; damage is fortunately less intense but also more widespread. Containment of a seeping or percolating liquid is difficult not so much because diffusion or dispersion is rapid, but rather since the spilled material becomes more or less inaccessible.

Failure of lateral or vertical control leads to damage to the environment. Some of the consequences of this loss are worthy of discussion. For gases and volatile materials, air pollution is perhaps the most obvious consequence. Likewise, for spills of liquids on the earth, damage to the area affected will be quite apparent. There is, unfortunately, more subtle and less immediate damage to the environment, particularly to the water ecosystem.

When a spilled hazardous material is washed into a sanitary sewer, the toxic effects of chemicals can upset the biological process of the municipal waste treatment plant, resulting in both the toxic spilled material and untreated sewage being discharged into a receiving stream or body of water. In the event that a spill is flushed into a storm sewer, the material usually flows unimpeded to the nearest stream. Thus one sees that accidents in municipalities cause direct and indirect insults to the water ecosystem. Further, spills that occur some distance from watercourses can be washed or flow into streams directly. On-land spills can seep into ground waters and endanger the public health of individuals and communities utilizing wells and springs. Toxic effects of land spills can be realized months after the actual occurrence of the spill when the contaminated ground water recharges the surface streams.

To the extent that the spilled or converted material in a watercourse is hazardous, fish kills and other less noticeable damage to aquatic biota will occur. Use of polluted river water for irrigation may cause damage to crops and soil and may also introduce the pollutant into a food chain.

Contamination of water supplies results in numerous sublethal effects on all living things, including man. The effects of long-term exposure to sublethal dosage is generally unknown, but carcinogenesis and mutagenesis could occur.

Perhaps the most common effect of pollution in watercourses is oxygen depletion effects (enhanced BOD).

Aesthetic damage and general nuisance effects of pollution are aspects that are less readily quantified but are ones that cannot be disregarded or neglected. In fact, damage to water use as a place for sports such as boating, fishing, and swimming is a factor that has contributed strongly to public concern about environmental protection. Disagreeable conditions include visible floating material, suspended or settled solids, discoloration or excessive turbidity, evolution of gases, especially hydrogen sulfide, blooms or high concentrations of plankton, and surfactants that foam when water is agitated or aerated.

General Aspects of Containment

In discussing the containment of hazardous material spills, one must consider what is included in the class of hazardous materials, whether the material is a liquid, a solid or a gas or liquefied gas, what the weather conditions are, where the spill occurred geographically, and whether fire or explosion hazards exist. According to the Water Quality Improvement Act of 1970, oil is excluded from the class of hazardous polluting substances, and the control of pollution by oil is handled under a special section of the Act. The designation of specific substances as hazardous pollutants by the Environmental Protection Agency has not yet been promulgated. However, one may expect that substances as diverse as acids and alkalies, tannery wastes, pesticides, and a large roster of the inorganic and organic materials of commerce (liquid ammonia, zinc cyanide, benzene, molasses) could be included.

To add perspective on the containment of spills of hazardous materials, one might profitably consider various aspects of containers and of containment before a spill has occurred. In a rather general and not mutually exclusive categorization, containers can be classified by:

1. Site: indoors or out-of-doors
2. Facility: in plant, in the field, in storage, in an open refuse pile or pit, behind a dike
3. Mobility: fixed, in a moveable container, in transit
4. Mode of transportation: truck, railroad, barge, ship, pipeline, airplane
5. Relative to ground level: on, above, or below
6. Nature of surrounding surface: prepared (concrete, blacktop, compacted) or natural (earth, water)
7. Physical or processing conditions: (a) pressurized, atmospheric, or under vacuum: (b) heated, cooled, stirred, aerated
8. State: in process, in storage, moving in pipes, in transit
9. Container type: tank, barrel, bag, box, reactor vessel, package, dike, Dewar flask
10. Type of container material: metal, glass, plastic, paper, burlap
11. Structure of container: (a) open-top, sealed-impervious, mesh (b) encased, single wall, composite or multiple wall
12. Operation: in process, during loading or unloading

This listing is intended to show the great diversity of situations under which spills can and do occur. Obviously, there is a great disparity in ease of containment following a spill depending whether it occurs: (1) at the plant during processing, loading or unloading where countermeasure equipment should be readily available or (2) in the field or during transit where containment or control devices or equipment are mostly unavailable immediately. Additionally, during the actual course of spillage, one should consider in what quantity and for how long the material will: (1) remain in the original concentration in the original container, (2) be confined in an equally concentrated form in an auxiliary container or behind a dike, (3) flow over a surface and collect in natural depressions, (4) reach and be diluted by a watercourse or be dispersed by wind, rain, or explosion.

Complete collection of the concentrated hazardous material from a spill and confinement of the material without hazard to human life or to the ecosystem is an ideal in any containment scheme. In practical cases, except under unusual conditions, the priority of active countermeasures would reflect the ideal: halt the flow, contain as much of the material in the most concentrated form as soon as possible, contain or inactivate spreading material or material that has entered a watercourse.

For coping with the wide spectrum of spills—based on container, material, location, and quantity—a catalog of spill containment techniques is advantageous. The list should include tried and proven methods, as well as novel approaches. An endeavor that can be undertaken to uncover new techniques is to list operations that can be performed on the two elements of containment, namely, the container and the contents. The results of such an attempt follow.

Operations that can be performed on the container include:

1. Rebuilding or reintegrating the container by reassembling, shoring up, re-enforcing, pulling separated parts together
2. Building a substitute container by:

   a. Forming dikes from earth, sandbags, wate-inflatable bags
   b. Assembling a knock-down container such as a plastic swimming pool or an inflatable boat-like device
   c. Using collection or confinement devices (booms, curtains, skimmers, portable dams) when a spill reaches a watercourse
   d. Digging, and preferably lining, a pit
   e. Blocking a sewer downstream from point of entry of spilled material
3. Repairing the container by:
   a. Patching with foam or boiler patches
   b. Solidifying or freezing the contents at the leak
   c. Adding something to the material in the container, i) that collects at the leak (make an internal patch or barrier from rags or wadding added to the liquid in the container) or ii) that congeals at the leak (a commercial antifreeze reportedly has this property)
4. Making geometric changes in position: up-end or rotate a leaking liquid or solids container so that the leak is on top or adjust the position of a container filled with a fluid so that the rupture is in contact with plastic earth (clay, wet concrete)
5. Bagging or otherwise entirely enclose or encase the container
6. Attaching a collection bag at the place of the leak.

Operations on the contents of the container can be more diverse. In the particular case of liquids escaped from the container, some operational procedures on the fluid are:

1. Changing fluid properties (physical changes) by:
   a. Converting to a solid through gelling or freezing
   b. Vaporizing or gasifying (possibly followed by burning)
   c. Increasing viscosity to retard spreading
2. Reticulating by:
   a. Soaking up or immobilizing with sponges, adsorbents or absorbents
   b. Adding magnetizable particles and applying a field
3. Converting chemically by sequestering, neutralization, precipitation
4. Diverting to a sump, or pump to a suitable container
5. Blocking flow at the entrance to a sewer or watercourse through diking or dam building
6. Consuming on site by burning (subject to stringent requirements of no significant air pollution
7. Layering or cover over to retard evaporation.

Obviously, this cataloging of operations is quite incomplete but serves to demonstrate a technique for developing novel containment methods.

As emphasized before, except under unusual conditions of public health and welfare, concentrated effort should be expended to contain a spilled material. In so far as is practical, containment methods should be designed so that they facilitate clean-up and restoration over a minimum area.

Containment of Spills of Volatile Substances

Generally, spills of gases or of readily volatile substances cannot be easily contained, though some attempts can be made to plug the leak in the container, transfer the material to another container, or render the substance less hazardous through some chemical reaction as the material is released.

For spills of flammable materials, precautions must be taken to prevent unintentional ignition by flames, hot objects, or sparks from arcing or discharge of static electricity. Foam covering may be of value in retarding the evaporation of liquids. In some cases and with due consideration for the maintenance of air quality, the material can be consumed by on-site burning, with the probability and consequences of explosion properly evaluated. When burning is chosen, it is usually the lesser of evils but not a really positive, desirable procedure. The case of confinement or inactivation of spills of volatile hazardous materials requires almost individual discussion, as the following remarks indicate. A chlorine spill could possibly be mitigated by reaction with photographer's hypo. Acidic oxides like those of sulfur and nitrogen could be coverted to acids by treatment with water followed by subsequent inactivation with bases. Adsorption on charcoal may be possible in some cases. Spills of gaseous or liquefied hydrogen cyanide, cyanogen and cyanogen chloride might be treated by reaction with basic oxides or with alkaline solutions, preferably chilled. Hydrogen fluoride could be reacted with silica gel; ammonia, with an acidic material; carbon monoxide, with some copper compounds. Carbon monoxide, as well as the more volatile hydrocarbons like methane, ethylene, and even ethylene oxide could be burned and, with proper precautions, would not pose a significant air pollution problem. Many volatile substances, such as carbon monoxide, chlorine and hydrogen cyanide, are toxic to humans and to other living species. The most prudent procedure for spills of these substances is often the evacuation of people and sealing off of the area. This is a type of inverse containment, where the material is unconfined but people are contained instead. One can regard the donning of gas masks and of protective equipment in a similar vein. There certainly is loss of control of the spilled material when people have to be "contained" while the hazardous material is free.

Containment of Spills of Solids

In the absence of bad weather, fire, explosion, and contact with other spilled reactive materials, solids will usually be self-containing. The lack of inherent mobility, which is characteristic of solids as contrasted with fluids, improves the prospects for maintaining lateral and vertical control. Further, solids are more frequently packaged and shipped in smaller containers—bags and drums—rather than in tank cars or truck tankers or by pipeline. Indeed, there might be advantages from the standpoint of environmental protection, as well as from the view of preserving human life, in requiring that all highly toxic substances be shipped in small, sturdy containers—even though the materials are used in large quantity.

Containment of a spilled solid in the most concentrated form usually requires only collection by shovelling or vacuuming. Suitable protective equipment for personnel may be required. There are obvious complications in spills of solids such as phosphorous pentoxide, phosphorous pentasulfide, dyes, ammonium nitrate, mercurials, arsenicals, and certain insecticides, rodenticides and pesticides, which are chemically reactive, explosive or toxic.

When a solid is fluidized, containment become more difficult. In situations where solids are dispersed by wind or explosion or solubilized by contact with rain or with the water used in flushing debris or in fighting fire, practical containment efforts may be limited to preventing run-off into sewers or streams. When the spill of a solid hazardous material is accompanied by fire, containment can be quite difficult and the consequences grave. Volatilization and combustion are frequently incomplete. Particulates and noxious reaction products are formed and dispersed. The heating or burning of solids such as ammonium nitrate, inorganic chlorates and perchlorates, and highly nitrated aromatics (picric acid, dinitrophenols) may result in explosion.

While it appears at first sight that containment of spills of solids should be relatively simple, the preceeding discussion shows that environmental conditions, carelessness, and bad practices can at times make the spill of a solid as harmful to the environment as that of a gas or a liquid, and containment as difficult.

Containment of Spills of Liquids

It is with spills of hazardous liquids—and the class includes slurries and fluidized mixtures in process—that the more difficult but nonetheless often tractable problems arise for containment and localization in concentrated form. As previously mentioned, the general advantages of containment are essentially three-fold: (a) reduction in local environmental damage, (b) reduction in extended damage, such as to watercourse, and (c) greater ease of collection, conversion, or detoxification. Approaches to achievement of these purposes will be discussed for general and for specific cases.

Containment on Land

Retention in the most concentrated form of liquid hazardous materials during actual spilling can be approached in several ways. There are two fundamental options: (a) stop flow from the leaking original container, and (b) collect the material in an auxiliary tank or sump, or confine the material in an auxiliary tank or sump, or confine the material with a barrier either on land or in a watercourse, as required. In an almost trivial case, the mere closing of a valve or shut-down of a pump may stop the flow, as may application of a suitable "Band-Aid" to a leaking hose or application of some sort of putty or packing to a joint or valve. Another way to stop the leaking of liquid from a container is to plug the leak, possibly with a crude boiler patch. The Rocketdyne Division of North American Rockwell Corporation, under Environmental Protection Agency Contract No. 68-01-0106, is addressing itself to this problem of stopping leaks in containers and is developiing field-use, foamed or resinous, quick-setting materials that can be applied over leaks and ruptures in a wide variety and configuration of containers and under a broad range of circumstances, even underwater. Figures 1 and 2 are artists' conceptions of potential applications for these leak plugging materials. Resistance of the foam or resin to attack by the leaking hazardous material and degree of permanence of the repair are important aspects of the methods to be selected.

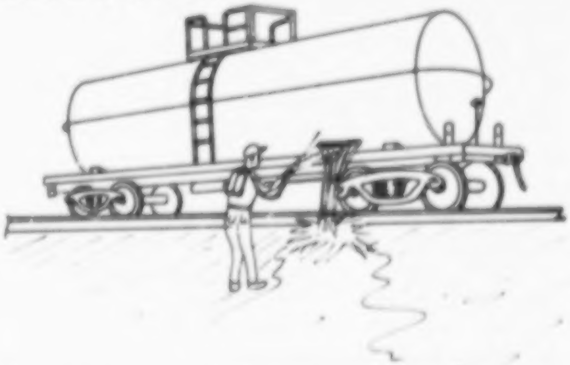

Figure 1: Foamed Plug for Sealing Leaking Containers on Land

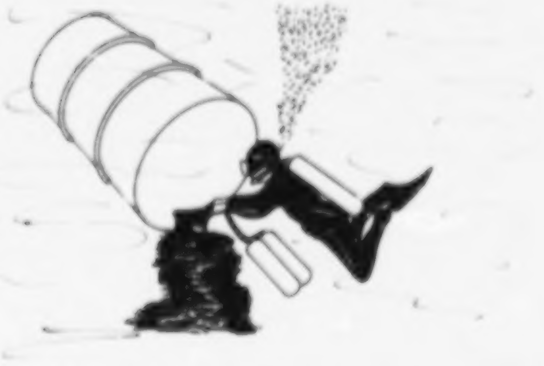

Figure 2: Foamed Plug for Sealing Leaking Containers Under Water

When the leak cannot be stopped at the source, the spilling liquid can be allowed to flow by gravity to a natural sump (creating a flow channel may require hand shovelling or machine trenching). On the other hand, some sort of artificial containing barrier can be created to confine the liquid, such as a dike on land. Prevention of entrance of a hazardous material—especially a soluble one—into a watercourse is extremely important.

When the spilled liquid is held in a natural sump or confined by a dike, the hazardous material can subsequently be pumped into a suitable auxiliary container. Residuals can be physically or chemically treated in place, as is appropriate. Treatment of the material that seeps into the earth poses special problems and emphasizes a common disadvantage of diking, whether achieved by forming a wall with portable or mechanized earth-moving equipment or from water-inflated or sand bags. The disadvantage is the absence of an impervious bottom barrier layer to prevent percolation into the earth (vertical spreading). In some fortuitous circumstances, the spill can be confined on a prepared surface (concrete, blacktop). Earthen surfaces and dikes, however, are prone to absorb spilled liquids. In special cases it may be possible to install plastic sheeting or shielding to minimize this seeping tendency. In this regard, Cornell Aeronautical Laboratory, Inc., under Environmental Protection Agency Contract No. 68-01-0110, is presently developing a sprayable, impervious sealant for preventing percolation into the earth.

The actual construction of earthen dikes is in itself a weakness in their use, for suitable dike-forming equipment may not be available and close approach to many spills by unprotected personnel can be hazardous. Removel of the material confined by an earthen dike generally requires that a sizeable quantity of earth must be removed as well. Disposal and/or reclamation presents a serious problem.

Under Environmental Protection Agency Contract No. 68-01-0100, MSA Research Corporation is developing portable equipment for construction of highly expanded, foamed plastic dikes. The rationale for using foamed dikes is chiefly ease and rapidity of set-up. Figure 3 shows how a truck tanker operator equipped with a back-pack type of unit might build such a containment wall, which has the advantage of confining the spilling liquid in its most concentrated form. Preliminary investigations by MSA indicate that concrete-based material can also be foamed in this novel approach to emergency containment. Adhesion of the foamed dikes to wet or dry earthen or prepared surfaces, reactivity of the foam with the spilled material, and operator protection are all important factors under consideration. MSA is also currently investigating the use of foamed plastics as a cover to blanket and inactivate pooled spills.

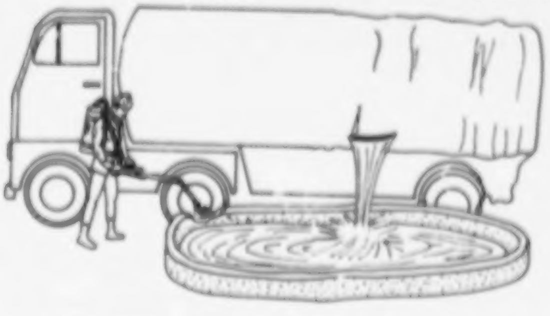

Figure 3: Foamed Dike for Containing Land Spills

Containment in Watercourse

When a spill of a hazardous material occurs in such a way that the material (liquid or fluidized solid) enters a watercourse, the problem of containment in the most concentrated form is exceedingly difficult.

For insoluble floating hazardous materials, the techniques applicable to oil spills may be suitable. These methods include the use of booms, flow guides, curtains, absorbers, and skimmers. However, when the spilled floating material is flammable, like benzene or some cyclic hydrocarbons, the ever present dangers of explosion and fire must be recognized. These hazards also exist when a flammable material is flushed into a sewer, which can be looked upon as an enclosed watercourse. Even when a flammable liquid can be kept out of a watercourse and confined on land—laterally to halt spreading and vertically to prevent evaporation—dangers of accidental ignition and explosion remain. Knowledge of flash points and explosion limits are of value, but often evacuation of people is the most practical countermeasure.

For materials that sink in water, certain types of underwater dikes may be useful. Long-term hold-up of creosote and of chlorinated hydrocarbons on the bottom of streams may produce serious ecological damage to aquatic bentha. Removal by vacuuming or dredging can be utilized, but this may produce local ecosystem damage, and the problem of disposing of the detritus remains.

When a water-soluble, hazardous material enters a watercourse either by direct spillage or run-off or from entrainment in underground water supplies, containment can be quite difficult. Alternate approaches, such as in-place reaction or adsorption can be attempted. Cornell Aeronautical Laboratory, Inc., Rex Chainbelt, Inc., and Battelle Memorial Institute are studying such procedures under Environmental Protection Agency contracts.

Ocean Systems, Inc., under Environmental Protection Agency Contract No. 68-01-0103, is developing a containment device that can be installed in a watercourse. Figure 4 is a representation of one type of application for such a device. The unit which may be regarded as a sealed boom" consists of a plastic curtain with a floatable collar and has provision for attachment to the bottom of a stream or body of water. Floatable material is confined above the watercourse surface, sinking material is immobilized at the bottom, and the solution resulting from dissolution of a soluble hazardous material is confined within the sealed boom. Appropriate inactivation or collection techniques can then be applied. Time and ease of deployment of the curtain are critical. Behavior in swiftly moving or turbulent streams or under impact with floating debris may limit applicability.

The problems of collection, re-concentration, and detoxification of a spilled hazardous material that has entered a watercourse especially point out the need for initial containment of the spill in the most concentrated form. The ounce of prevention is costly, but the pound of cure is much more so, particularly when damage to the water ecosystem is considered.

SUMMARY

In this paper, emphasis has been placed on the advantages of containment of hazardous material spills in their most concentrated form. The idea of containment was correlated with the concept of control, and that of a spill, with the loss of control—both lateral and vertical.

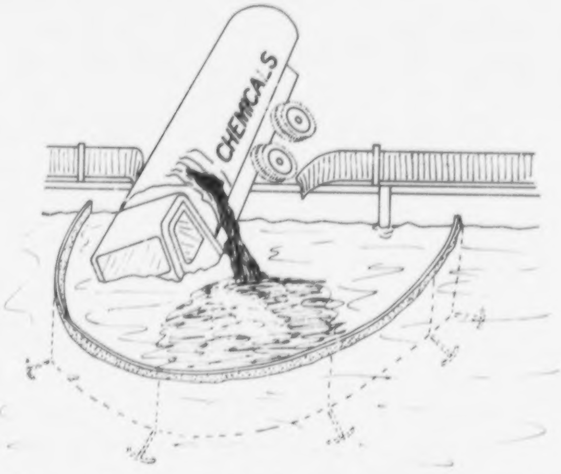

Figure 4: Sealed Boom for Containing Spilled Materials In Watercourses

The advantages of prompt containment of spills are: (1) minimization of damage to the total environment, (2) facilitation of on-site clean-up operations, and (3) prevention of dispersion into watercourses through flow into sewers, run off into streams, and percolation into the earth with subsequent seepage into sub-surface water supplies. Generally speaking, the greater the spreading of a spilled material, the more extensive the environmental damage. That clean-up and restoration are facilitated by containment of a spill in concentrated form becomes quite clear when one reviews the significant problems of collecting or inactivating a material that has been dispersed in a watercourse.

A number of techniques for containment of spills of hazardous materials are currently under development by Environmental Protection Agency contractors; these techniques include: physical barriers for deployment in watercourses, foam diking, and emergency plugging of leaking containers. By functionally analyzing the two major elements of containment, i.e., the "containing device" and the "material contained", it is possible to develop potential approaches for other methods of containment.

THE PHYSICAL CONTAINMENT OF LAND SPILLS BY A FOAM DIKING SYSTEM*

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INTRODUCTION

It is immediately obvious in considering hazardous chemicals that the principle deterrent to the damage of the ecology from such materials is the strict control of their manufacture, storage and transportation. The first step, of course, is strict rules designed to prevent the spills of such materials. It is obvious, however, that even the most stringent rules will not completely eliminate the possibility of accidental spills. Within plant sites and storage facilities mechanisms are available to contain accidental discharges of these materials such that they cannot damage the surroundings or reach local waterways. The greatest problem would appear to exist in the transportation mode.

With respect to spilled materials reaching water, there is probably little that can be done if such accidents occur during water transportation. With land vehicles, however, there are potential solutions which would tend to minimize, if not eliminate, the possibility of such spilled materials entering adjacent water systems.

In past efforts, MSAR has been associated with two programs to study the problems of hazardous chemical spills in unconfined areas. The first was concerned with the spill of liquid rocket fuels in field complexes; the second with spills or leaks of chemical warfare agents during transportation or in the field. In both of these studies it was clear that immediate action had to be taken if there was any hope of containing or controlling the spill at all. Three basic steps were considered: (1) sealing of the leak if possible, (2) containment of the spilled material and (3) physical removal of the spill.

It was concluded from these studies that control of the spill of the hazardous chemicals from transporting vehicles must be considered as one major area in the prevention of hazardous chemical materials from damaging the water ecosystem. Based upon our prior work and our current knowledge in these areas, it was our belief that the available technology would allow the successful evolution of both portable and mobile systems which could provide containment of spilled materials at the site of the accident either through dikes or flow-diverting barriers. Technology was also available to provide in situ generation of surface covers to prevent vapor losses from such spills. Completely contained, the spilled material can then be cleaned up by a number of techniques.

Dikes and Barrier Systems

In considering the erection of dikes or diversionary barriers the initial thought is usually to natural materials. Although significant use should be made of natural barriers and depressions by diverting spills toward them, their use to construct dikes or other barriers pose a number of problems. Not all types of surface materials are amenable to the formation of dikes of any significant height. When the ground is frozen or water soaked, movement by hand is difficult if not impossible, and under the worst conditions even heavy equipment may not be sufficient.

To provide a general purpose system operable under all of the environmental conditions to be experienced, it becomes necessary to consider structures built up out of artificial materials. Whether these materials form an enclosure or divert the flow

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*This work sponsored by The Environmental Protection Agency under Contract No. 68-01-0100.

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of spilled materials, the basic requirements are the same. Materials should be resistant to chemical attack and fire retardant if not inflammable. Most important, maximum benefit should be realized from as small an amount of material as possible using portable or mobile equipment with small power requirements.

In assessing the requirements, the limiting value would appear to be the necessity of obtaining large quantities of material rapidly from small portable or mobile systems. These conditions appear best satisfied by materials which can be foamed or expanded. At present two materials classes possess the basic requirements. These are polymer foams and so-called foamed inorganic materials.

Alhough a large number of polymers can be produced in the foamed or expanded condition, only polyurethane appears to possess the necessary characteristics for field operable units. Formed by the xothermic reaction of two materials, the heat generated volatilizes and expands a reaction product or an added blowing agent which creates the foam. Polymerization occurs at the same time, setting the foam to a rigid mass. The only power necessary is pressure to expel and blend the two components. Other polymer foams require mechanical agitation and/or are open cell and thus a porous medium.

There is a broad spectrum of inorganic materials which can be produced in light weight form by blending them with a preformed detergent or protein foam. The major item in this class at the present is foamed concrete. Foamed gypsum is also an available material, as well as sodium silicate foam. The latter, however, requires mechanical agitation, is partially open-cell and subject to hydrolysis.

Once contained, rapid clean up of the spill is almost mandatory. Vapor release to the air and seepage into the ground continue to constitute a significant material loss which poses immediate problems to the surrounding environment. Groundwater movement can transport spilled material into the water system.

Large exposed surfaces of spilled chemicals also pose an immediate threat, in terms of toxicity and flammability, to the personnel attempting to control and clean up the chemical. Isolation of the chemical surface along with control of boil-off would appear to be desirable. The surface covering should be such that it does not interfere with the clean up operation. In the past year foam has been shown to be effective as a surface cover to isolate and control vaporization rate of selected chemicals.

Polyurethane

Of immediate concern for the control of hazardous chemical spills is the availability of a small portable system which could be carried on the transporting vehicle and utilized by the carrier personnel. Polyurethanes, already commercially available in a portable foam dispensing system, potentially offered a quick response solution. The available item of commerce in a man-portable size delivers some 35 cu ft of foam at an expansion of 25:1 with an output of approximately 1 cfm/min. Current nozzle designs are directed to intimate mixing to achieve the high quality foam needed to serve the current applications. The restricted output due to this mixing is far from adequate for diking application.

For a useful system to evolve for the control of hazardous chemical spills, improvement of the rate of delivery is required. It is also necessary to concurrently determine the ability of polyurethanes to block materials falling in the hazardous chemical category. In the beginning the program was directed to improving the delivery rate of the foam and the evaluation of the material's ability to block hazardous chemical materials.

Increasing the flow to some 3 to 5 cfm per minute was reasonably readily accomplished. As stated, the low flow rates of existing systems are directly due to the mixing vanes within the nozzle. Intimate mixing is only necessary if a high quality foam is to be generated. For the control of spilled materials, foam quality probably can be compromised to some degree without impairing the material's ability to perform its function. Shortening the mixing helix, the enlarging the nozzle orifice 2.5 times, flow rates as high as 7 cfm per minute initially could be achieved, with an average of 4-5 cfm/min. These changes still allowed generation of an acceptable foam.

With the availability of the higher delivery rates, evaluations were started on the ability of the polyurethane to dike liquids. Early tests showed the available polyurethane to have limitations. On dry surfaces such as cement and asphalt, effective adhesion could be achieved to contain heads of water of several feet. A drum-like circular form of polyurethane foam 36 inches in height and 30 inches inside diameter set up on concree was maintained full of water without leakage for a period of days.

Similar bonding action could be achieved on dry ground. The ability to contain liquids behind barriers built on this substrate, however, depended upon the firmness of the soil. On hard packed materials effective control is achieved. On loose soil however, the fluid eventually worked a path through the soil beneath the barrier. The time required to compromise the barrier is dependent on the liquid head and the rate of flow, and even in loose soil a measurable delay time can be effected.

The polyurethane foam performed poorly, however, on vegetated ground and wet surfaces. On vegetated ground the quick frothing action of fluorocarbon-blown foam resulted in bridging over the vegetation with no penetration to a firm substrate. On wet surfaces, including asphalt and concrete, the adhesion of polyurethane was poor and penetration of the blocked fluid through the interface was fairly rapid. The only effective seals on wet surfaces occurred where the foam could be locked in place. Figures 1 and 2 shows urethane used to block a curb type storm sewer drain. Interlocking into the grading overcomes the problem on wet surfaces.

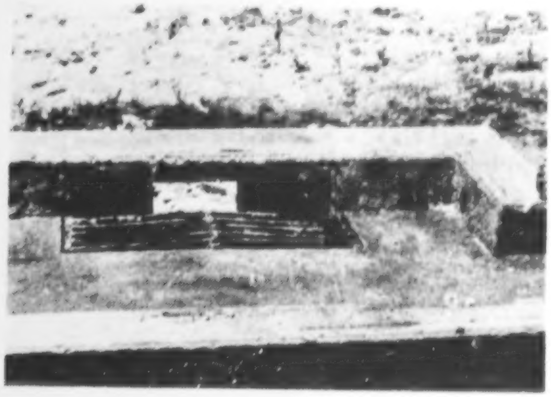

Figure 1: Curb Drain Set in Concrete

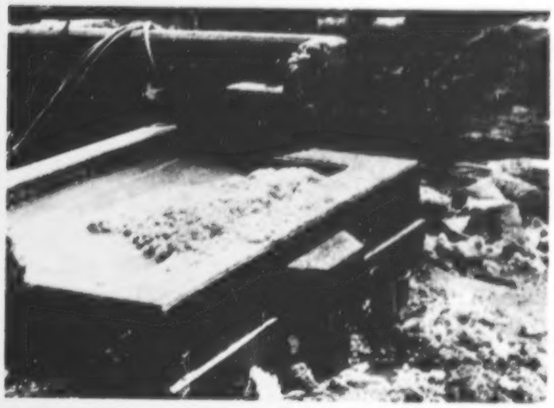

Figure 2: Urethane Block Sealing Storm Drain Against Liquid Flow

In an effort to improve the situation with vegetated ground and with wet surfaces, an extensive investigation of foam formulations was undertaken. The difficulty with vegetated ground proved resolvable by slowing down the foaming action. This was accomplished by switching almost completely from the normal blowing agents to methyl chloride. With methyl chloride, the material as sprayed is a liquid with medium viscosity and has a measurable delay in the onset of foaming varying from 10 seconds upward, depending upon the temperature of the substrate. This time delay allows the material to flow down through the vegetation to the solid substrate. This type of system does require some additional pressurization. The volatile fluorocarbons are desirable in the pressurized portable systems as pressure sinks and a final system will have to make a compromise between the frothing of freons and the weight of gaseous nitrogen systems. Unfortunately, as yet the difficulties of the wet substrate have not been resolved.

During the course of the formulation studies, water was given consideration as the blowing medium since it normally reacts with isocyanate to form CO_2. This was not a satisfactory solution of itself since the use of water detracted substantially from the normal adhesive characteristics of the foam. It gave rise to a new material however, one resembling polyurethane but employing only isocyanate and water as the basic constituents. In this form expansions as high as 200/1 could be achieved while still providing a rigid foam material. Although the basic material was not satisfactory, extensive property modification became possible by the incorporation of water-soluble polymers into the water side of the reaction. To date, by use of these water-soluble materials the adhesive characteristics of the isocyanate water system have been significantly enhanced. Investigation of this combination of materials is continuing with the hope that other inherent limitations of the polyurethane materials can be corrected.

Concurrently with these efforts, evaluations were being conducted on the chemical compatibility between polyurethane foam and selected hazardous chemical materials. These selected materials included methanol, acrylonitrile, phenol, chlorine, ammonia and acetone-cyanohydrin. As was expected, with the exception of methyl alcohol, the foam once blown and rigidized was essentially unaffected by these materials. With the present formulations of polyurethane methyl alcohol rapidly soaks into the foam destroying its effectiveness in blocking that material.

Aside from temperature effects which are a problem with low boiling materials such as ammonia and chlorine, none of these materials adversely affect the ability of the polyurethane formulation to form foam. Pools or flowing streams of these materials, however, behave in the same manner as a wet surface preventing adhesion. Thus, at the present state of development, it is not possible to block a flowing stream directly. To block or divert a spill it is necessary to erect the barrier ahead of the flow on a dry surface.

At the present time efforts with the standard polyurethane are being completed with the determination of its limitations and capabilities. Work is continuing with the isocyanate-water system with hope of improving adhesion on wet surfaces and resistance to a wider range of materials.

Inorganic Foam Systems

Foamed concrete and associated materials such as foamed plaster and gypsum, like polyurethane, are well developed materials of construction. These materials are formed by blending already formed, low expansion foam into the appropriate slurry. The resultant material is then applied or formed in the same manner as it would be if the foam had not been added. Because of the viscosity and the finite set time required, forms or other means of containment must be utilized until a sufficient set has occurred. Resultant expansions are quite low, between 2 and 5/1. In the case of concrete this represents a change of density from the normal 150 pcf per cu ft to as low as 30 pcf per cu ft density. The reasons for using foamed rather than normal density materials vary depending on the application, but total weight is always a predominant factor. This, along with logistics, is a basic factor in this program also.

In considering these materials for the dikes or dams, the concept is of a mobile unit which might be carried on a rail car or transported to the scene of the accident after the fact. Truck mounted units for both mixing and application are widely used in the construction trades at this time. The basic problem in adapting these materials to the application at hand is the inability to build-up these materials without some form of constraint. This phase of the program was directed to the incorporation of a gelling mechanism into concrete or other inorganic materials such that an instant set could be obtained. Since these gelled structures would have a minimum of shear strength prior to the onset of hardening, the barrier heights which could be built-up rapidly were a function of the material density. By using foamed systems the density problem could be held to a minimum.

The initial approach taken to obtain the gel formation was by the incorporation of water-soluble polymers into the slurry which could subsequently be gelled by some chemical means. Work in this direction was quite unsuccessful. We were using commercially available equipment both for the formation of the slurry, the foam, and the subsequent blending and dispensing of the final mixture. Some of the better polymer systems for incorporating gelling, such as polyvinl alcohol, although soluble in water, have long dissolution times that require the application of heat. Other polymer systems had equally difficult situations such as control of pH or delay times in gel activation. None of these were acceptable situations for a field operable unit, where ready mixing and simple operations are mandatory.

Due to the difficulties being experienced with the water-soluble polymers, a concurrent program was initiated to investigate the feasibility of achieving a quick set using silicate additions to cement slurries. The initial success realized with this approach forced abandonment of the water-soluble polymer technique. With the silicate a variety of slurry mixes comprised of combinations of cement, gypsum, fly ash and bentonite were tried. The best product was developed using the silicate addition to simple Portland cement-water slurries.

After investigating a wide range of water-silicate-cement compositions best results were shown to be obtained from the composition Portland cement-silicate-water, although bentonite did show promise as a further additive. At mix ratios of 4 to 1 cement to silicate weight ratios, structures were erected between 12 and 16" high with angles of repose in excess of 40°. The cement slurry is mixed approximately 2 to 1 cement to water and the silicate slurry 1.5 to 1 water to silicate, both by weight. Preformed foam of 20 to 1 expansion is added at a rate of some 20-25 gals per 100 lbs of slurry. The initial set time of the material is 2 to 4 seconds with an ultimate density of 30-35 lbs/cu ft.

The gel strength was the limiting value in determining the height which could be built up. Some further improvement has been realized by adding bentonite into the mixture. Its primary action is to increase the viscosity of the slurry without impairing the balance of the other materials. Its concentration must be limited to 5% of the total slurry weight. At the present state of development 30 lbs per cu ft concrete structures can be built to heights in excess of 2 ft with angles of repose in excess of 45 degrees. The height and angle of repose limitations are still a function of the gel strength of the concrete. Figures 3 and 4 are typical of the types of structure which have been used to evaluate foam concrete systems. They are built up very rapidly and completed before any cement set can occur. Further heights could be added if time was available to allow some cement set to occur.

Work is still underway on this material. It is primarily directed to the incorporation of fibers, which might be able to provide better green strength to the structure as formed, and further decreases in density, both of which would be advantageous to the formation of higher barriers. Work must also be conducted to insure that the material is compatible with the various hazardous chemical materials it might encounter if it is to be used as a material of construction for dikes and dams.

Film Covers

The use of high expansion foam to cover spills to reduce the hazard therefrom has only a limited prior

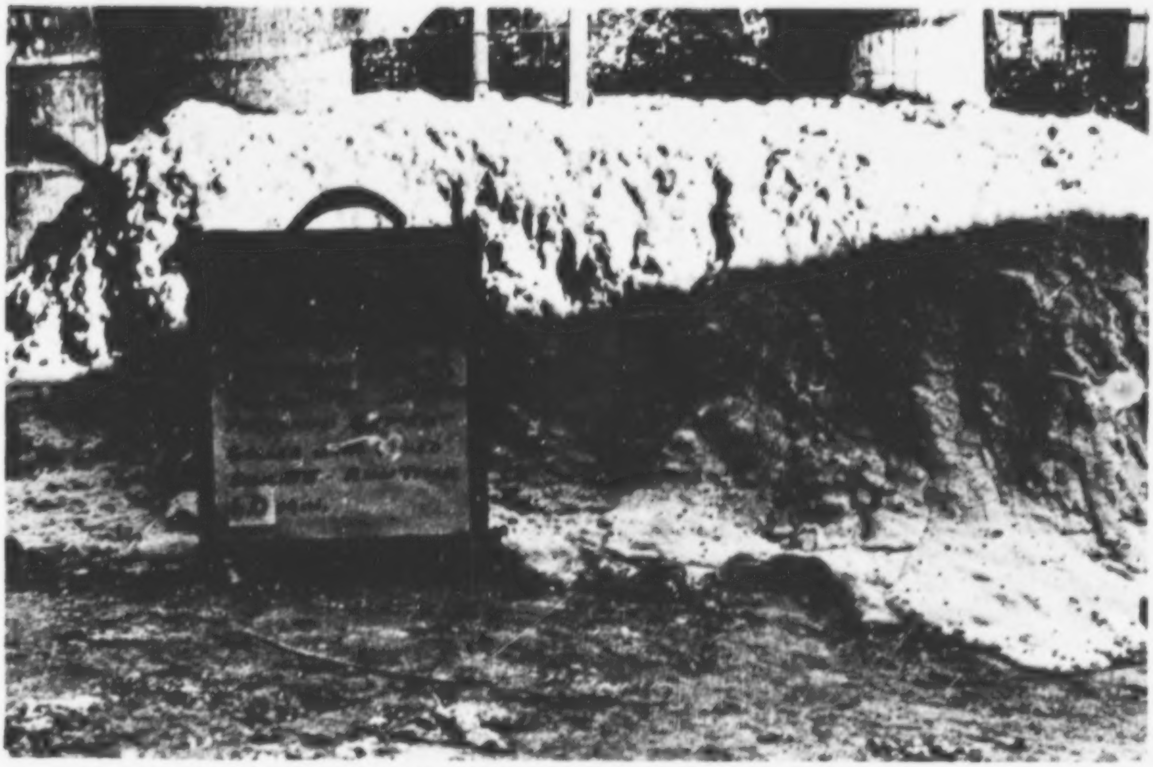

Figure 3: Face View of Foamed Concrete Barrier 20 in. High by 18 in. Wide by 6 ft.

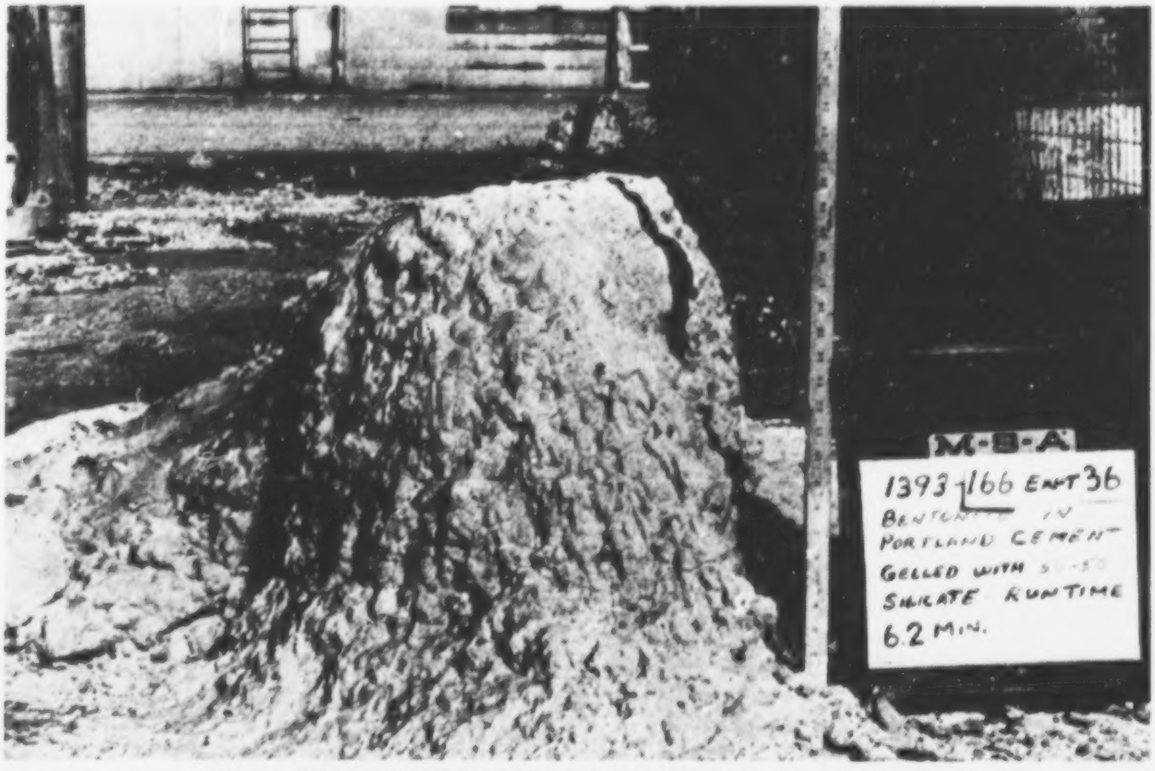

Figure 4: Side View of Foamed Conrete Barrier 24 in. high Showing Steep Angle of Repose

history. High expansion foam of the fire fighting variety has been used in the field to cover gasoline spilled from a tank truck. Subsequent work by MSAR in the laboratory verified the fact that the foam did effectively modify the gasoline surface to control vapor release and prevent ignition by sparks or open flames in the area. The possibilities of foam in this area have been further demonstrated by the control of spills of vinyl chloride and liquid ammonia. Control of both of these compounds required modification to normal foam to provide for an extended life, but with these modifications vaporization rates of these materials were reduced to 50% of the boil-off rate under identical conditions without a cover. These results were sufficiently encouraging to pursue the use of high expansion foam as a protective cover on hazardous chemical spills.

It was realized early in the program that probably no one foam would be capable of controlling all materials. The actual situation that was encountered was unexpected however. With modifications of the long life of foam it was possible to control the majority of materials previously listed. It was not possible however to retain a high expansion foam cover over polar solvent type materials for more than a few minutes with even the best of the so called long life foams, both those of MSAR and others who are active in the field. A screening program was instituted to reevaluate water soluble polymeric material as foam additives to compensate for the detrimental affects of the polar solvents. Initial attention was directed to the synthetics, and some small improvements were noted with acrylates and acrylamides. It was not sufficient to be useful, however.

The failure of the synthetic materials to provide any benefit effected a shift to the natural occurring water soluble polymeric materials. Few if any of these materials, however, could be added in any significant concentration without adversely affecting the viscosity of the subsequent solution to the point that high expansion foam could not be generated with conventional equipment. Such viscosities could be handled in flooded plate type foam generators, but they were not considered suitable for field use. It became necessary therefore to consider lower expansion ratios if these materials were to be employed.

Before proceeding to lower expansion systems, mechanisms were investigated for forming films on the liquid surface. These represented systems in which the foam drainage would either gel or chemically react with the polar solvent or otherwise form a film over the surface to reduce the intimate contact of the foam with the compound. This included investigating the current technology of the so called light water film forming fluorocarbon surfactance. Some improvement was realized with a few systems, but again, life was measured in the matter of minutes rather than the hours considered necessary. Effective systems peculiar to a single compound were found. In the case of methyl alcohol, sodium silicate-phosphate combinations in the foam effected a gel surface layer. Due to their limited activity they were set aside at this time.

The poor results of each of the above efforts shifted the program to lower expansion systems and the investigation of natural gel forming substances. These included gelatin and starch derivitives, gums, a number of trade name materials of natural origins, and representatives of the current generation of protein foam materials available commercially. Although several of the materials in this category have shown promise, maximum results have been obtained by the use of pectin. Tests to date show this material to be completely compatible with methyl alcohol, acetone, acylonitrile and the remainder of the materials elected for study in this program including ammonia and chlorine. Initial indications of the effectiveness of the pectin fortified material were derived from the fact that normal high expansion foam could be built up over methyl

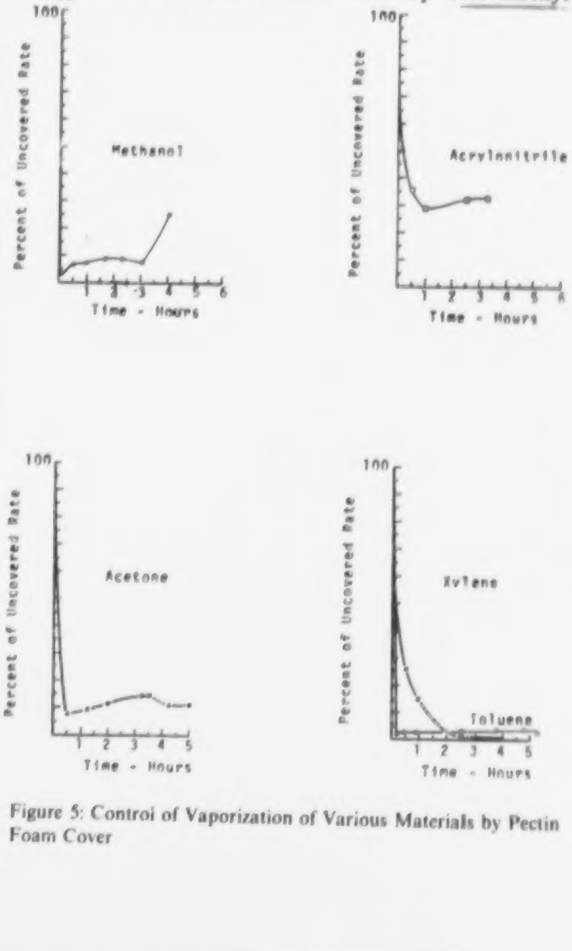

Figure 5: Control of Vaporization of Various Materials by Pectin Foam Cover

alcohol if a thin layer of the pectin materials was first applied to the surface. Laboratory tests have now been run with a cross section of materials using the pectin foam to assess the actual surface control effected.

In these tests foam was made at 50:1 expansion from a water solution of 2% pectin and 3% sodium lauryl sulfate. It was applied over the surface of each material contained as a 1" deep pool. Continuous measurements were made of the concentration of each chemical in the vapor phase above the liquid by sampling an air stream flowing over the surface at 3 ft/minute. Figure 5 shows the effective reduction of the vapor concentration by the pectin foam, by plotting the instantaneous concentration with time as a percentage of that experienced with no cover. With hydrocarbons, toluene, xylene, etc., the concentration is rapidly reduced below 1%. For methanol and acetone the effective reduction is to 10%. Acrylonitrile is the most difficult, being reduced to only 30% of its normal concentration.

At the present time a large field demonstration unit is being fabricated to allow testing on a larger scale under more realistic conditions.

A PHYSICAL BARRIER SYSTEM FOR CONTROL OF HAZARDOUS MATERIAL SPILLS IN WATERWAYS

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ABSTRACT

Ocean Systems, Inc., under contract to the Environmental Protection Agency, has developed a physical barrier for containing hazardous materials spills in waterways. The barrier is designed to contain a wide variety of soluble and insoluble materials leaking from stationary sources up to 50 feet in length, in waterways up to 25 feet in depth with currents up to two knots.

The barrier is constructed of a highly flexible fiber-reinforced plastic and incorporates an air-inflated flotation collar, which supports the barrier, and a water-inflated seal, which seals the barrier to the bottom of the waterway. The barrier is maintained in position by a mooring system that employs lightweight explosive embedment anchors. Only a small amount of auxiliary equipment is required to deploy the barrier.

The paper describes the system and deployment techniques and presents the results of full scale field tests of a prototype system.

INTRODUCTION

Industrial production of hazardous polluting substances is constantly increasing. Even though there is increasing care during production and transportation of these substances, accidental spills of these substances into the nation's waterways have and will occur at an increasing rate. In many instances, the nature of the spill is such that its containment is possible, thus reducing the danger to the water ecosystem.

Ocean Systems, Inc. has developed for the Environmental Protection Agency, under Contract No. 68-01-0103, a physical barrier system for containment of hazardous material spills in waterways. This paper describes the development and testing of a prototype of this system. It should be noted that the system to be discussed has not been designed to contend with all types of hazardous substances and all spill situations since the general intent of the program was to demonstrate the feasibility of a physical barrier system rather than to develop an optimized system.

Problem Analysis

In selecting a containment barrier as the most desirable countermeasure against spilled hazardous materials, a number of possible steps for dealing with spills were evaluated against criteria suggested by the Environmental Protection Agency. Table I summarizes this evaluation and shows that physical containment of spilled substances offers the greatest potential in dealing with spills occurring in waterways.

Subsequent to selecting a containment system as the most desirable countermeasure, a number of containment methods were investigated. These included earthen dams, formed-in-place plastic dams, chemical dams (such as gel-forming additives), cryogenically formed dams and mobile inflatable plastic barriers.

After investigating these methods, Ocean Systems, Inc. selected the inflatable plastic barrier as the most desirable method to develop for use in water-

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(Note: The sixteen highest priority hazardous substances are specified in this publication.)

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TABLE 1

Evaluation Matrix for Spill Countermeasures

X = Meets or can meet evaluation criteria

COUNTERMEASURE	EVALUATION CRITERIA Applicable to Various Watercourse Types (open sea, estuaries, etc.)	Minimum Auxiliary Equipment	Reasonable First Costs	Light in Weight	Rapidly Applicable in Congested and Remote Areas	No Secondary Damage to Environment	Safe to Handle by Untrained Personnel	Treats to Proper Water Quality Level	Applicable to Wide Variety of Spill Types
Neutralize Acid with Base	X	X	X				X	X	
Neutralize Base with Acid	X	X	X				X	X	
Form Solids or Less Toxic Compounds	X	X	X					X	
Powdered Activated Carbon	X						X		X
Physically Remove Bottom Seeking Compounds	X	X	X		X		X		
Boom and Skim Floating Compounds	X	X	X	X	X	X	X		
Aid Natural Dilution			X	X	X		X		
Contain Soluble Materials to Prevent Diffusion	X	X	X	X	X	X	X	X	X
Burn off Floating Volatiles		X	X	X	X				

ways. The other candidate systems were rejected for a number of reasons, the most notable among these being cost, excessive amounts of required auxiliary equipment, difficulty of deployment and inability to function in a flowing stream. Ocean Systems believes the selected concept can be developed into a lightweight, rapidly deployable containment system useful for a wide variety of spilled substances. Other advantages of the concept are that it minimizes the volume of water which must be treated, and once in place it extends the time period over which the spill can be treated. These factors permit a safer and more effective ultimate treatment or disposal of the contained substance.

Technical Analysis

Before a detailed design of the barrier system could be completed certain basic design parameters had to be established. To obtain these parameters a series of technical analyses were conducted. In brief, it is sufficient to say that the most important analyses defined structural requirements of the barrier, mooring forces and deployability; however, because of insufficient published experimental data the solutions are only approximate. Field testing of the system will provide the exact answers.

Design Concept

The design concept consists of a highly flexible fiber reinforced plastic barrier that can be deployed around a spill source as illustrated by Figure 1. The top of the barrier is supported by an air-inflated flotation collar and the bottom of the barrier is sealed against the bottom of the watercourse by a liquid-inflated seal. The barrier is maintained in position by a mooring system that employs lightweight explosive embedment anchors.

The barrier system may be conveniently divided into three subsystems: the barrier subsystem, the mooring subsystem, and the deployment subsystem, each of which is described.

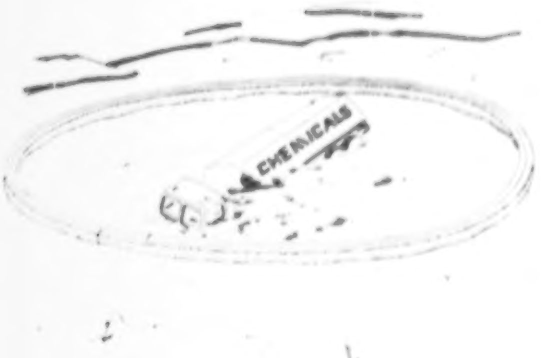

Figure 1: Deployed Barrier

Barrier Subsystem

The barrier is an impenetrable wall that completely surrounds the spill source and spans the water column from the bottom to the surface of the waterway. Its basic dimensions, 200 feet in length and 30 feet in height, enable the barrier to completely surround smaller spill sources such as tank trucks, and individual tank cars in watercourses having depths up to 25 feet. Because the design is modular, multiple lengths of barrier may be joined together where a longer barrier is required (such as for multiple tank cars and barges). Salient features of the barrier design are illustrated in Figure 2.

The flotation collar consists of two parallel air bladders, each of which is divided into two compartments for a total of four separate air-inflatable compartments per barrier unit. When inflated, the two parallel air bladders have a combined buoyancy of about 200 pounds per linear foot of barrier. Approximately 150 pounds of this buoyancy is required to maintain the barrier upright in strong currents of about 2 knots. The remainder is reserve buoyancy that keeps the top of the barrier above the water surface; however, if current velocities approach about 2.5 knots the entire collar will submerge, thus preventing further strain on the mooring system so that the barrier will not be torn from its moor and swept away. The bottom portion of the barrier contains a 25,000 lb breaking strength belt that transmits forces from the barrier wall to five anchor points that are equally spaced around the bottom of the barrier.

Also incorporated in the bottom of the barrier is a large bladder which runs for the entire length of the barrier. This bladder is used to effect a seal between the barrier and the bottom of the watercourse. The seal is required because it is not possible, in most cases, to moor the barrier tightly against the bottom, and also because of irregularities in the bottom itself. The seal is normally inflated with water, but is more effective when inflated with heavy solutions, liquids, mixtures, or slurries. Because the barrier is normally deployed with the anchor points to the outside and with the bladder on the inside of the barrier, heavy liquids or solutions contained inside the barrier will tend to create pressure against the bladder, thus making it more secure against the bottom.

Both the air and water bladders are inflated from the surface through hoses. Relief valves set at 1/2 psi prevent the bladders from overpressurization within the inflation rates of the compressor supplied with the system.

A detachable vertical joint is provided in the barrier wall. This joint makes the barrier modular and also permits the barrier to be opened up for deployment around spill sources that protrude above the surface of the waterway.

This joint can be seen in Figure 2 where the ends of the barrier are reinforced with a strength belt through which grommets are placed at close intervals. Rope is used to lace the ends together forming a joint that has a strength exceeding that of the barrier wall. To prevent the contained hazardous substance from leaking through the joint, a seal is provided to cover the joint. The seal is in the form of a flap of material that is permanently attached to one end of the barrier with Velcro hook and loop fastener. As with the bottom bladder, the seal flap is also located on the inside of the barrier when deployed.

The material selected for fabricating the wall and bladders of the prototype barrier is a nylon filament reinforced plasticized, polyvinyl, chloride fabric known by the trade name "Herculite 20". It was selected because of its high strength to weight ratio, good chemical resistance, relatively low cost and ease of fabrication and repair. The fabric weighs less than 11 oz per square yard and has a tensile strength of over 110 lbs per inch of width. Its abrasion resistance is more than ten times that of comparable strength cotton canvas. The woven nylon filaments impart a high tear resistance to the fabric; punctures will not spread into running rips. Herculite 20 is approved by the California Fire Marshal, the New York City Board of Standards and the National Fire Prevention Association as a flame retardant. The fabric is also approved by the U. S. Coast Guard for various uses.

The fabric's resistance to environmental weathering is very high. It can remain operational from 210° to -65°F; ice will not adhere to the fabric. As with most vinyl based chloride resins, it is extremely corrosion and chemical resistant, although the plasticizers (added for flexibility) are attacked and extracted by certain solvents, oils, and chemicals. The resistance of Herculite fabric to the sixteen

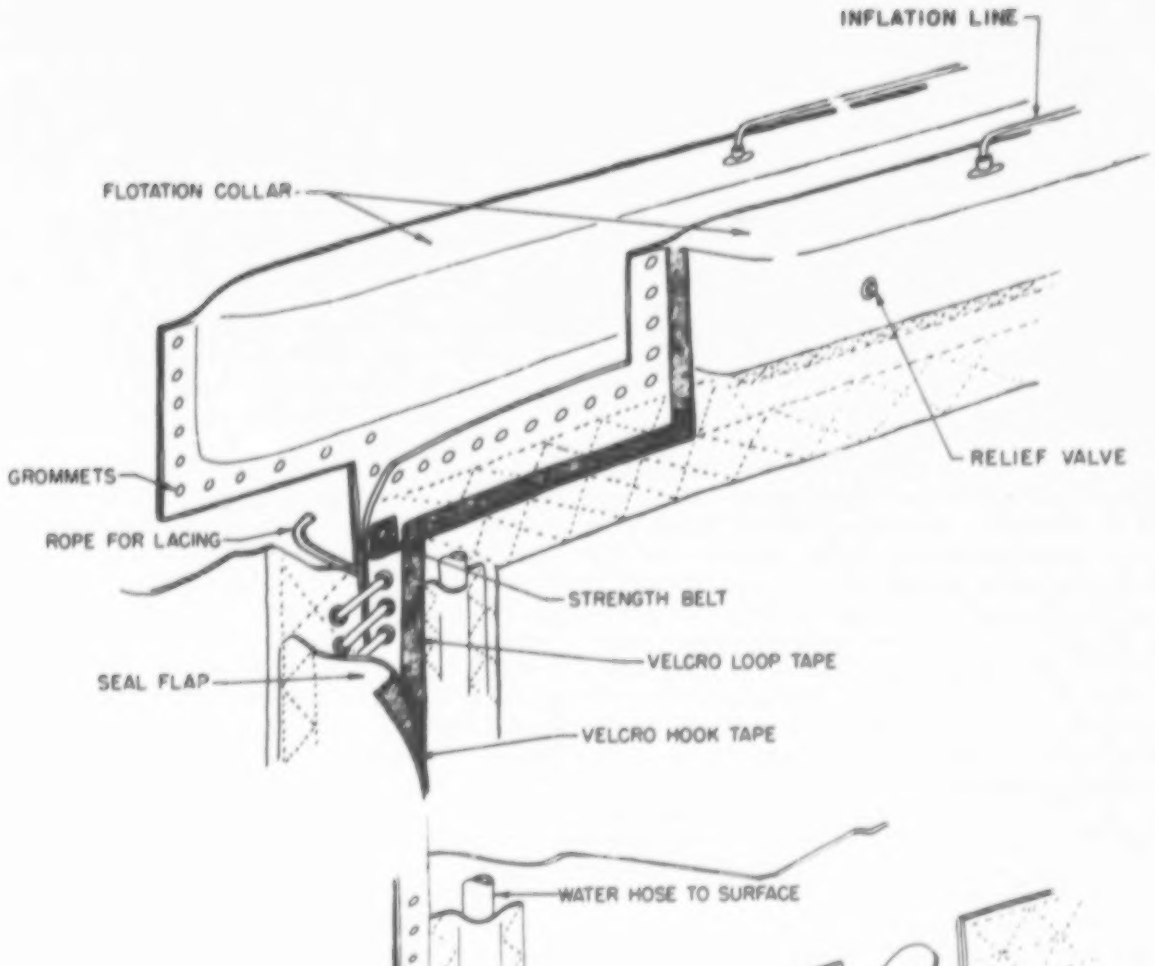

Figure 2: Details of Barrier

highest priority soluble hazardous polluting compounds is given in Table 2.[1]

Most of the cordage, hardware and fastening materials used in the barrier is either nylon or PVC. The chemical resistance of PVC is, of course, similar to the Herculite fabric rated in Table 2. Nylon is also rated in Table 2 against the sixteen highest priority compounds. Nylon has a high resistance to weathering in outdoor and marine applications, and has good resistance to chlorinated hydrocarbons, strong

TABLE 2

Chemical Resistance of Barrier Materials

CHEMICAL	Herculite Fabric with Plasticized Polyvinyl Chloride	Nylon Line
1. Phenol	A-B	A
2. Methyl Alcohol	A	A
3. Insecticides, Rodenticide, Cylic	A	A
4. Acrylonitrile	A	
5. Chlorosulfuric Acid	A	A-B
6. Benzene	B	A
7. Ammonia	A	A
8. Misc. Cylic Insecticides	A	A
9. Phosphorone Pentasulfide		
10. Styrene	B	
11. Acetone Cyanohydrin	A	
12. Chlorine	A	
13. Nonyi Phenol		A
14. DDT	A	A
15. Isoprene	A-B	
16. Xylenes		A

A = Satisfactory for Use
B = Satisfactory in Certain Circumstances
C = Unsatisfactory
* where a rating is not given, the chemical resistance is unknown

(Note: These ratings are for chemicals in concentrated form. Resistance will be better for dilute forms.)

bases, weak acids, alcohol and organic solvents. It is attacked by strong acids and bleaching agents.

All fabric seams in the barrier are electronically welded and reinforced with stitching. This method of joining can be readily used to fabricate a barrier of the same design from any one of a number of different materials. Thus, barriers resistant to almost any chemical could be fabricated using a standard design.

Mooring Subsystems

Five explosive embedment anchors manufactured by EDO Western Corporation are used for mooring the barrier. Explosive embedment anchors were selected for the mooring subsystem because of their very high holding power to weight ratio. The anchors used in the system weigh about sixty lbs (including weight of firing gun), and have a rated vertical pull-out strength of 10,000 lbs for sand and mud installations. The same anchor system is also available in a configuration suitable for soft rock installations.

The complete anchor, ready to fire, is illustrated by Figure 3. The anchor is fired electrically from the surface. A hydrostatic safety device arms the gun automatically when it is submerged a sufficient distance beneath the water's surface. When the gun is fired the anchor point penetrates the bottom trailing a 1/2 inch diameter wire rope pendant which is attached to the anchor point and serves as the mooring cable. The firing gun and stand are recoverable and can be reused.

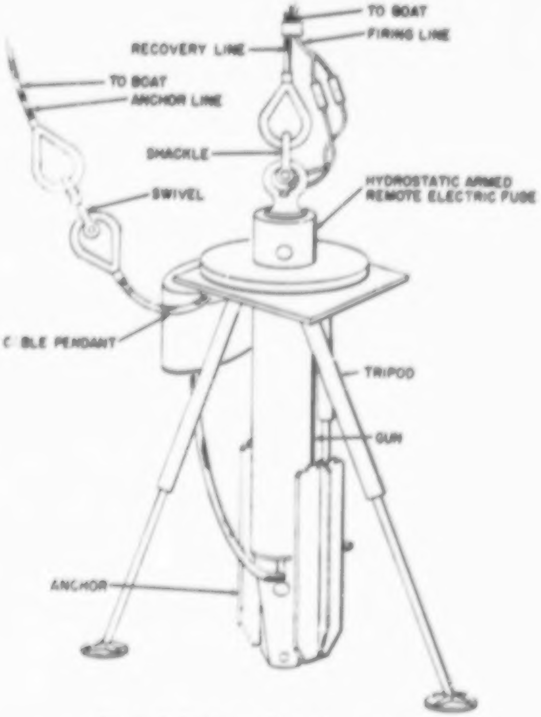

Figure 3: Explosive Embedment Anchor

Because of the reaction distance required by the gun when the anchor is fired, the anchor, as presently designed, cannot be fired in water depths less than about 10 ft. However, because the firing charge is small (162 grams), a small boat can be as close as 20 feet to the anchor when fired. The explosive shock of the anchor firing may create hazards with certain shock sensitive chemicals, but at this time the problem has not been investigated.

Other anchoring systems such as drilled-in and jetted-in anchors are completely compatible with the barrier system, although transportation and auxiliary equipment requirements make their use less desirable. Also, they may require considerably more time for installation. In situations where, for some reason, the explosive anchors cannot be installed, deadweight anchors can be used as an emergency anchoring system.

Deployment Subsystem

The deployment subsystem includes special devices for pulling the barrier to the bottom, an air compressor/water pup for inflating the barrier, vessels for deploying the barrier and marker buoys and anchors for temporarily mooring the barrier.

The individual items of the deployment subsystem and their functions are best illustrated by considering a typical deployment scenario. For instance, assume that a trailer truck laden with a hazardous material has plunged into a waterway. It is completely submerged, but has been located and marked, and is known to be leaking the hazardous substance into the waterway.

1. The barrier arrives at the spill scene aboard a pickup truck. (Previously, the barrier was prepared for deployment by joining the ends together, folding it accordian style from top to bottom and taping it at six-inch intervals with tape of a known breaking strength. Also, a small amount of foam flotation and a ripcord for breaking the tape have been provided under the tape for the full length of the barrier. Figure 4 illustrates a section of barrier prepared in this manner).

2. As three men unload the barrier into the water from the pickup truck, two other men are unloading a small boat equipped with a davit from a second truck that has arrived with auxiliary equipment.

3. Thirty minutes have elapsed since the deployment team arrived at the spill scene. The small boat, with two men aboard, is now towing the barrier from shore to the leaking truck. The other men are busy unloading the remaining equipment and preparing the explosive anchors for deployment.

4. The men in the small boat are now positioning the barrier above the spill source. Sections have been lifted over the marker buoys and temporary anchors are being attached to the anchor points on the barrier.

5. The barrier is now positioned in a taut pentagonal shape above the spill source by adjusting the five temporary anchors.

6. One hour has elapsed and small boat returns to shore and picks up the first explosive anchor with its davit.

7. The first explosive anchor is transported to the moored barrier and is lowered to the bottom at a point directly under an anchor point on the barrier. The anchor point has a marker buoy attached so that it is easily located.

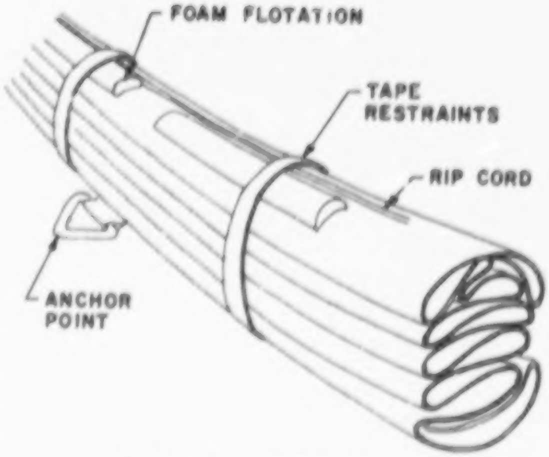

Figure 4: Section of Folded Barrier

8. The first anchor is fired into the bottom. The firing gun is recovered and the wire rope pendant from the explosive anchor is temporarily attached to the anchor point on the barrier. The marker buoy supports the weight of the wire rope and prevents the barrier from sinking. The remaining four explosive anchors are installed using the same procedure employed for the first anchor.

9. Two and one-half hours have passed since the arrival of the deployment team at the spill site. The small boat has now picked up five pull-down devices (Figure 5) from shore and is returning to the barrier.

10. Attachment of the first pull-down device begins. First the wire rope pendant is detached from the anchor point on the barrier and the eye on the end is cut off with a wire cutter. Next the pull-down grip and mooring grip are slipped on the cable. The cable is then put in a cable grip attached to the davit and pulled taut, after which the pull-down grip is allowed to fall down the wire rope to

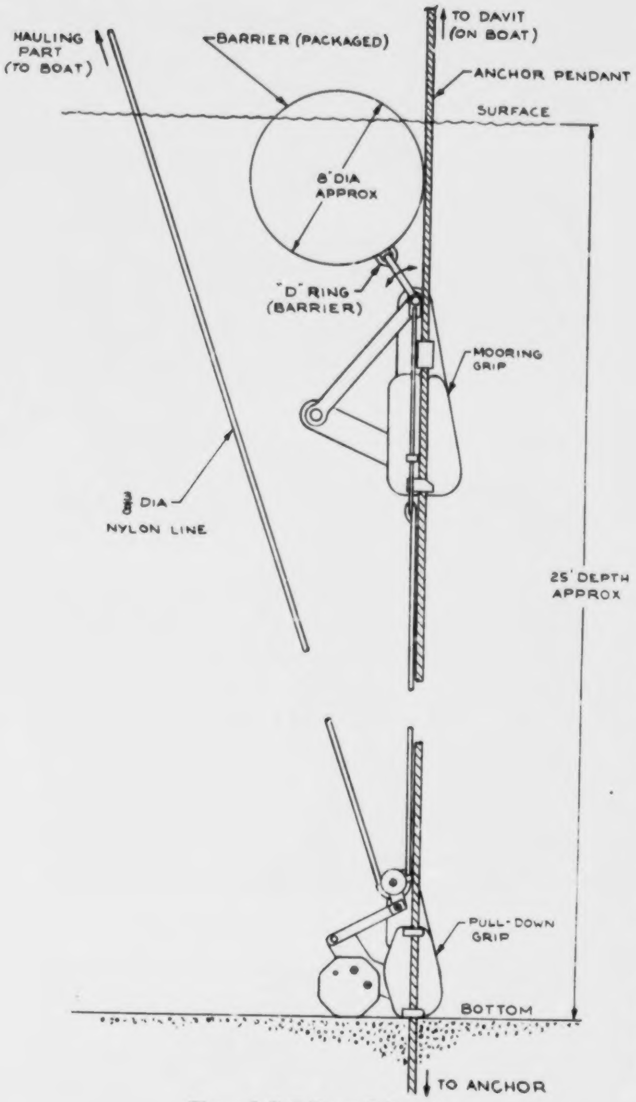

Figure 5: Pull-Down Schematic

the bottom. The pendant is then slacked and the mooring grip is attached to the anchor point. The remaining four devices are installed using this same procedure.

11. Three and one-half hours have now elapsed since arrival of the deployment team. Upon the installation of the fifth pull-down device the anchor pendant is left in the cable grip and the barrier is pulled to the bottom in the manner illustrated by Figure 5. The operation is repeated at each anchor point. After each anchor point has been pulled to the bottom, the ends of the wire rope pendant and pull-down rope are attached to the marker buoy that has been removed from the anchor point.

12. The small boat returns to shore and picks up the air compressor/water pump. A total of four and one-half hours have elapsed as inflation of the barrier begins. As air is pumped down to the barrier it gains buoyancy, breaks the tape bindings and begins to rise towards the surface. The rip cord is pulled to break the remaining bindings in order to shorten the time required for the barrier to rise to the surface.

13. Five hours after deployment began the barrier has risen to the surface and is effective in containing the leaking material. Inflation continues for another 45 minutes until the flotation collar is completely inflated.

14. Inflation of the water bladder begins, and at an elapsed time of seven hours after initiation of deployment the barrier is in place with all bladders inflated, and deployment is complete.

The elapsed times in the preceding example are realistic estimates of the time required to deploy the barrier under average weather conditions and considering small unexpected problems that might arise during deployment. Under very favorable conditions deployment time might be significantly less, and conversely, under poor conditions, or for deployment of multiple lengths of barrier, the time may be longer.

Prototype Field Tests

To date, two field tests of a prototype barrier have been conducted. The first test was in a lake at Sugar Grove, West Virginia; the second was in the lower Potomac River at Colonial Beach, Virginia. Prior to the field tests of the prototype barrier, the explosive anchors and pull-down device were tested at Bear Lake, Utah.

Bear Lake Test

In the field tests at Bear Lake, Utah, three test anchors were fired into a coarse silt bottom in water approximately 25 feet deep. Anchor penetration ranged from 13 to 21 feet. After each anchor was fired, a prototype pull-down device was installed on the anchor pendant and a buoy (which simulated the barrier) was pulled to the bottom. The anchors and the pull-down device functioned properly.

Sugar Grove Test

The objectives of the field test at Sugar Grove, West Virginia, were to test the barrier in quiet water conditions and develop deployment techniques. The test was conducted in a man-made, flood

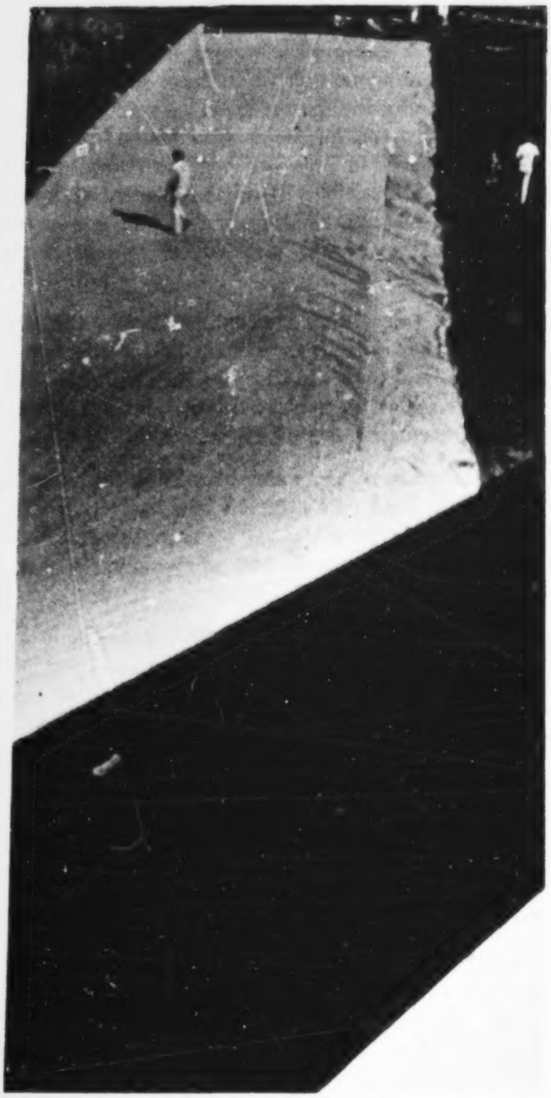

Figure 6: Barrier Spread Out

control lake approximately 9 acres in size. The lake varies in depth from very shallow at one end to approximately 20 feet near a dam and flood control gate at the opposite end. The average depth where the barrier was deployed is approximately 16 feet.

Deployment of the barrier began in a manner similar to the example deployment scenario. Figure 7 shows the barrier being transferred to the lake from a small van. The small boat shown in Figure 8 was used to tow the barrier into position around a marker buoy. Figure 8 also shows the barrier temporarily moored in a pentagonal shape around the marker buoy.

After the barrier was temporarily moored, two explosive anchors were fired directly below two of the anchor points on the barrier. Figure 9 shows one of these explosive anchors as it was being lowered to the bottom. Inspection by a diver revealed that both anchors had been damaged upon contact with hard rock underlying the silt bottom of the lake. Rather than fire additional explosive

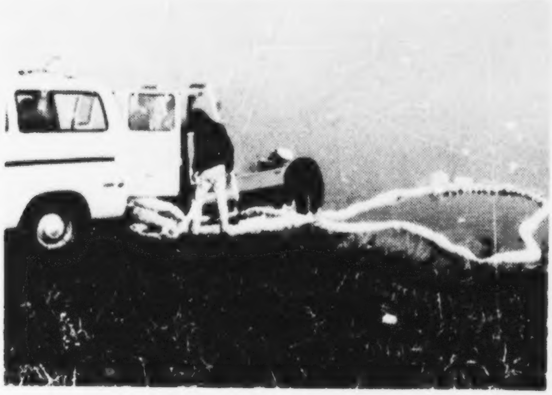

Figure 7: Barrier Being Transferred from Truck to Lake

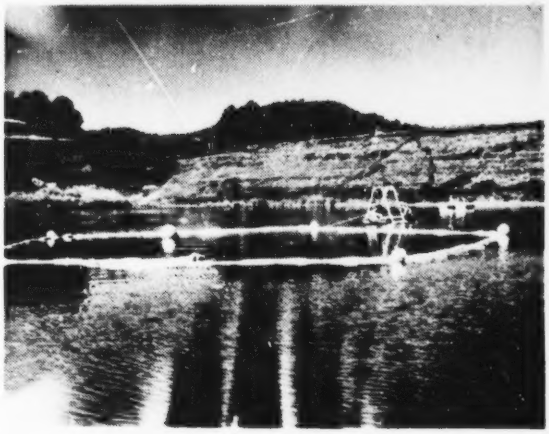

Figure 8: Barrier Moored with Temporary Anchors

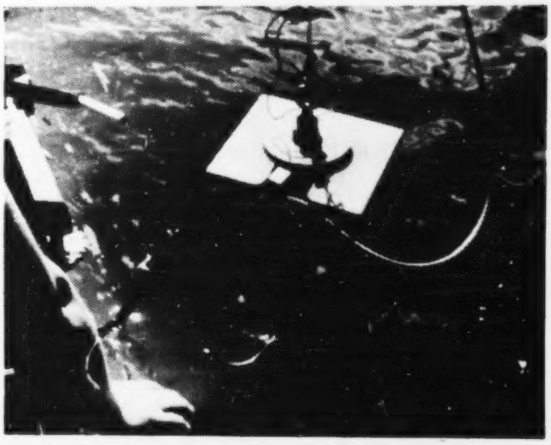

Figure 9: Explosive Anchor Ready for Firing

anchors with the possibility that they too would be damaged, clump anchors were used to simulate the explosive anchors. The test then proceeded as if the explosive ahcnors were in place.

Figure 10 shows a pull-down device being attached to the anchor pendant. The pull-down devices were prearranged on a flat board (as shown in Figure 11) so that they would not become tangled.

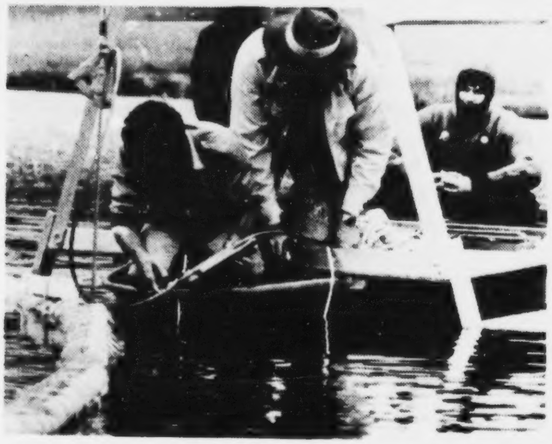

Figure 10: Pull-Down Device Being Attached to Anchor Pendant

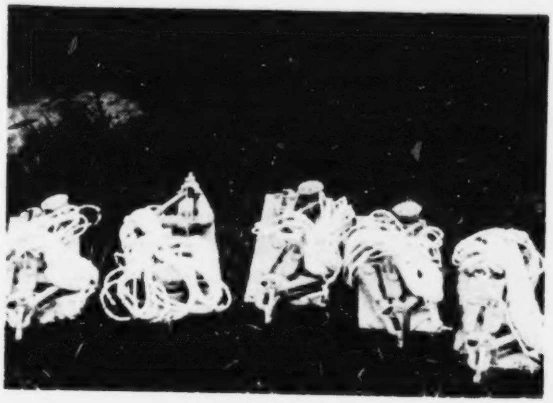

Figure 11: Pull-Down Devices Ready for Use

After all the pull-down devices were installed, the barrier was pulled to the bottom. The barrier was then inflated with the air compressor and in Figure 12 it can be seen rising to the surface. The water bladder was inflated as soon as inflation of the air bladder was completed.

Figures 13 and 14 show the barrier fully deployed. The flotation collar is not in a circular shape because of a breeze that was blowing at the time the photograph was taken. The collar was free to move since the barrier was deployed in water considerably less deep than the barrier's design depth.

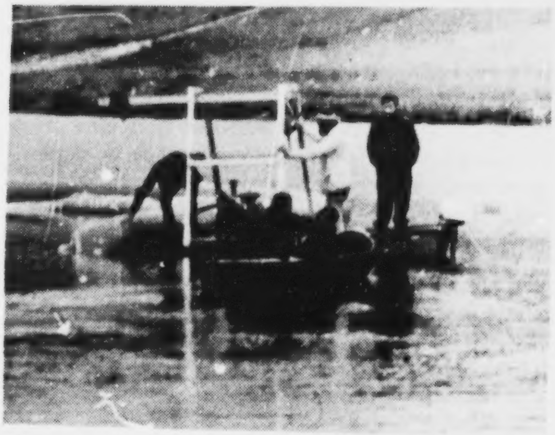

Figure 12: Barrier Being Inflated

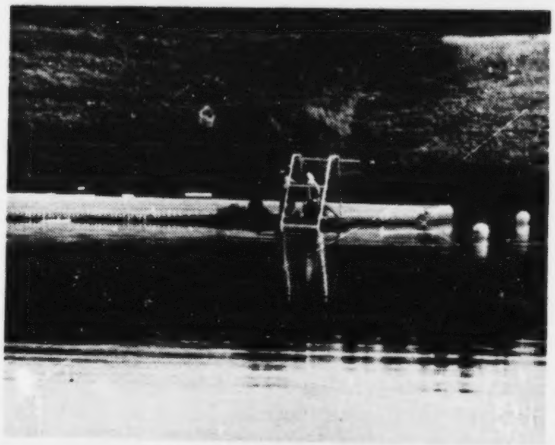

Figure 13: Barrier Deployed

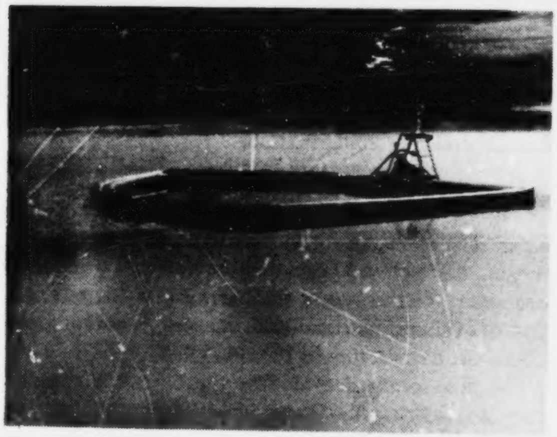

Figure 14: Barrier Deployed

After the barrier was fully deployed, enough Rhodomine-B fluorescent dye was injected into the contained water to form a 200 ppb solution (deep red) inside the barrier.

Samples of lake water from both near the surface and near the bottom were collected for the next 22 hours from a number of points close to the barrier. These samples were then analyzed for dye with a fluorometer (capable of detecting a few parts per billion), and it was determined that there had not been any leakage from inside the barrier.

The total time required to deploy the barrier was approximately six hours. This time is figured from the elapsed times for the different steps of deployment. The time required to install the mooring system was extrapolated from the time required to fire the two explosive anchors. The time associated only with testing was discounted.

Colonial Beach Test

The objectives of the field test at Colonial Beach, Virginia, were to further develop and refine deployment techniques, to evaluate the effectiveness of the barrier in containing a spill in a current, and to make quantitative measurements of the mooring forces and water velocity in order to assess the structural integrity of the barrier.

The test site was about two miles offshore in a very wide area of the Lower Potomac River. The barrier was transported to the test site aboard an 18 ft catamaran boat. The same small boat used in the lake test and an additional small boat were used to deploy the barrier in a temporary moor. Two explosive anchors were installed, both of which achieved deep penetrations in the mud bottom. Before additional explosive anchors could be installed, the weather began to deteriorate, with winds increasing to twenty knots and seas running 3-4 feet in height. Working from the small boats became hazardous, and, because there was no improvement in weather conditions forecast for the immediate future, the test was cancelled.

At the time this paper is being written, another field test of the barrier is being planned.

Results and Recommendations

The test at Sugar Lake demonstrated that the barrier is totally effective in containing a spill in still water. The ability of the barrier to contain a spill in a current has not yet been demonstrated. To demonstrate the effectiveness of the barrier in a current and also to evaluate its structural integrity, another field test of the barrier should be conducted.

The time required to deploy the barrier is reasonable, considering the steps involved in the deployment process. Although the deployment time can be reduced, Ocean Systems believes that the barrier cannot be deployed quickly enough to respond to spills where the entire amount of hazardous substance is leaked into the waterway in only a few hours.

Use of the barrier for containing transportation spills is limited to situations where the container is leaking at only a moderate rate, or where a leak has not yet occurred but where potential for leakage exists (e.g., in salvage operations). The barrier could also be permanently installed on the bottom in a passive mode at potential spill sites, such as transportation terminals and pipe discharges, and inflation could be made automatic.

Deployment of the barrier system in sheltered water under favorable weather conditions is possible using small boats and a minimum number of personnel. In open water, especially in unfavorable weather, deployment is considerably more difficult, and may be hazardous using only small boats. In all cases where the spill site is close to shore, the barrier should be deployed from shore and towed to the spill site.

The field test at Sugar Grove, West Virginia, demonstrated that the anchor points intended for soft bottom will not penetrate rock. Since, in most cases, the type of bottom will probably be unknown, two sets of anchor points (one for soft bottoms and one for rock) should be included in the barrier system. Also, five complete ready to fire anchor assemblies would reduce the deployment time and, in addition, would afford the system greater reliability.

SUMMARY

Physical barrier systems can be used in hazardous material spill situations to contain the spilled substance and, because of their numerous advantages over other countermeasures, they should be the logical "first choice" countermeasure. Ocean Systems, Inc. has fabricated and field tested for EPA a lightweight, economical, rapidly deployable physical barrier system. The tests conducted to date indicate that the system is a viable solution; however, additional field testing should be performed to fully assess the feasibility of the system. Once this system is fully developed, Ocean Systems, Inc. believes that it will become a valuable tool for controlling pollution.

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METHODS FOR PLUGGING LEAKING CHEMICAL CONTAINERS*

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ABSTRACT

The progress of a current project is described. The eventual goal toward which this project is directed is to develop practical methods for plugging leaks in damaged chemical containers, through application of suitable plastic barriers, thereby making it possible to prevent water pollution from spilled hazardous chemicals. The feasibility of this concept has already been demonstrated, including sealing of many hazardous chemicals and application to leaks both underwater and in air. Scale-up tests are being made, and have included successful demonstrations in 55-gallon containers. As a consequence of the success already realized, it is predicted that a practical and useful system, embodying this approach, can be developed.

INTRODUCTION

In so highly an industrialized society as ours, tremendous quantities of chemicals are continually produced, usually at one location, and then shipped to another site for use in some application. Many of these chemicals are quite hazardous if introduced into natural waters. The likelihood of accidental release to the watercourses is obviously increased by the many sequences involved in the production, transfer, shipping, unloading, and ultimate utilization of the chemicals. Thus, it is not at all surprising that spills do occur.

Such spills can occur in a variety of ways. For example, the most dramatic, and generally most serious, type occurs when a container is violently ruptured (sometimes accompaied by fire or explosion), and large quantities of the hazardous material are spilled almost instantaneously. A less catastrophic spill results when the container maintains its integrity, but suffers enough damage to cause leakage of the hazardous material at a moderate rate. The leaking chemical can enter the watercourse either directly (for example, as the result of a barge accident or a land-based container falling into the water) or by flowing or being washed into a drainage channel or percolating into the ground water supply.

Countermeasures which neutralize or treat hazardous chemicals which are already mixed and in the waterway may require hours or days to be initiated and involve the very difficult problem of handling large volumes of water. Therefore, a vital need is for a system which can prevent further dissemination of the hazardous chemical by stopping the leak regardless of whether the container is on land or underwater. The Rocketdyne program is directed toward this need, with the underlying philosophy that it is far better and easier to prevent a hazardous chemical from entering a waterway than it is to try to remove it after entry.

Scope of Program

The original goal of the program was to demonstrate the feasibility of plugging and controlling spills of hazardous materials by application of suitable plastic barriers. Particular emphasis has been on methods for plugging leaks in damaged chemical containers. The major tasks involve: (1) screening tests to determine the suitability of various currently available plastics (used in the broad

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*Work sponsored by the Environmental Protection Agency under Contract No. 68-01-0106.

sense to include various rubbers, foamed systems, etc., in addition to polymer systems more normally considered as "plastics") as sealants for selected hazardous chemicals, (2) evaluation of parameters involved in sealing leaks with selected sealant/ hazardous chemicals, and (3) demonstration at the 5- to 10-gallon level of the feasibility of this approach. Because of the degree of success already achieved, the original scope of work is being modified to place greater effort on preparations for implementation and application of the concept, and to begin preliminary development work toward eventual operational use.

Progress To Date

Although the program is only at its midpoint (December 1971), significant progress has been made on each of the tasks, and the feasibility of the concept has already been demonstrated. The results obtained are described below.

Types of Sealant Candidates

The original approach to plastic barriers which would seal leaks and prevent further dissemination of the chemical into a watercourse was based on the use of chemical systems such as polyurethanes which would be forced into the holes in the container, and, by expansion, seal these leaks. As the program developed, it was concluded that an equally valid approach is the use of sealants which do not expand when forced into the holes (as do the polyurethanes), but rather are already of the proper size and provide suitable adhesion to plug these leaks. The foam approach has the advantage that the increase in volume on foaming allows for a tighter seal. However, the chemical reaction of the foaming may be inhibited or retarded by the ingredients in the container. The true "sealant" of the second approach is unaffected by this latter problem.

Another way of classifying sealants depends on specifying the number of components in the final sealant. For example, one-component sealants include polysulfide rubber, polystyrene Instant Foam, and swelled Neoprene W; two-component sealants include many of the urethane foams and the epoxy systems. Many of the two-component systems adhere to a variety of surfaces including painted metal, whereas the one-component sealants often produce a mechanical plug to seal the leak.

One-component sealants have the advantage of being ready to apply at the moment a leak is discovered, whereas the need for mixing two or more components entails a delay during which the hazardous chemical continues to contaminate the environment. However, one-component sealants do not necessarily form a permanent seal, and they must be reinforced by applying a more permanent seal such as that formed by a suitable epoxy or polyurethane sealant.

One concept for increasing the "bridging" capacity over that of the sealant itself is to provide some type of supporting fabric or fibers. A simple version of this concept has been tested and shown to be feasible—a "patching" technique in which the sealant is applied to a supporting fabric (e.g., nylon cloth) and the patch is then applied over the leak. This technique has been employed to reinforce a polysulfide rubber plug of a 2-inch hole at the bottom of a 5-gallon container.

Screening Tests

Initial screenng tests were made using 1/2-pint cylindrical paint cans as the container for the leaking liquid. The cylindrical can was painted with an alkyd resin enamel which is representative of the painted outside surface of large chemical containers. (Adhesion to an unpainted metal surface is generally greater than to a low surface energy painted surface.) Sealants that were effective because of their adherence to the outside of the leaking containers could therefore be screened on these small cans with assurance that their adhesion behavior on large-scale containers would be similar.

Holes of various sizes from about 1/8-inch to 3/4-inch diameter were punched near the bottom of the can, and the test hazardous chemical was poured into the can, while covering the hole temporarily. The cover over the hole was removed either in air or underwater, and the sealant candidate was applied as rapidly as possible.

Table I lists the materials screened as potential sealants and the results obtained. Because of this early success, the initial tests were soon expanded to include most of the hazardous chemicals that rank among the top 20 on the priority list.[1] Chlorosulfonic acid and phosphorus pentasulfide are probably too reactive with water or the sealants and would probably require a special sealant system. On the other hand, many of the other top 20 hazardous chemicals can probably be sealed with one or more of the sealant candidates that are effective with either benzene or phenol. For example, sealants useful for benzene leaks would also likely be effective against the other hydrocarbons, styrene, isoprene, xylenes. Sealants useful for phenol would probably also seal acrylonitrile and acetone cyanohydrin. The range of

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[1] Ira Wilder and Joseph Lafornara, *Control of Hazardous Materials Spills in the Water Environment: An Overview*, presented before the Division of Water, Air and Waste Chemistry. American Chemical Society, Washington, D.C., September 1971.

TABLE I

Potential Sealants Screened

Type of Material	Source	Indication of Results
Polystyrene Instant Foam	Monsanto	Very rapid foaming; no adhesion to metal; may be suitable for "mechanical" seal.
Modified (rubbery) polystyrene Instant Foam	Monsanto	
Polyvinyl acetate Instant Foam	Monsanto	
Urethane Foam	Nalge	Aerosol type cans give inadequate mixing and delivery; setting time probably too long to be useful.
Urethane Foam	MSA	Components promising, especially if modified for shorter setting time.
Urethane Foam (Durathane)	Expanded Rubber and Plastic	Setting time of basic components much too long; can be modified for shorter time.
Epoxy Putty (Polypoxy)	Pettit Paint	Setting time too long.
Epoxy putty (Epoxylite 3351)	Epoxylite Corp.	Setting time too long.
Epoxy Putty (Sea Goin'-Poxy Putty)	Permalite Plastics	Promising (shorter setting time still needed).
Steel-filled Epoxy Putty (Devcon SF)	Devcon Corp.	Sets up rapidly.
Lead-filled Epoxy Putty (Devcon L)	Devcon Corp.	Sets up rapidly.
Polysulfide Rubber Putty (EC612)	3M	One component.
Butyl Rubber Sealer (EC1202-T)	3M	One component.
Polyurethane Putty (Urabond)	Poly Resins	Sets up slowly on exposure to moisture or liquid water.
Swelled Uncompounded Neoprene Rubber	Rocketdyne Prep	

hazardous chemicals sealed or likely to be sealed with sealants already tested is shown in Table II.

The epoxies and urethanes tested, listed in Table I, are all base-catalyzed; acid interfered seriously with their polymerization and resulted in breakdown of already polymerized material. In general, these sealants, when set up, retain non-polar material, but are unsuitable for phenol and acrylonitrile. The Sea Goin' Poxy Putty and the metal-filled Devcon putties set up in a relatively short time, but needed some mechanical assistance (e.g., a solid material patch) to support the epoxy while it hardened.

The three different types of rubber tested are inert to phenol and swell or dissolve in aromatic hydrocarbons. The uncompounded Neoprene W was obtained from duPont, and was allowed to swell in either carbon tetrachloride or benzene, forming a relatively soft, highly pituitous mass before testing as a sealant. In this condition, it was stuffed into a two-inch diameter hole near the bottom of a 5-gallon

TABLE II

Hazardous Materials Considered, with Expected Results from Leak Sealing Tests

Hazard Ranking	Hazardous Material	Sealed by Available Sealants: From Tests Completed	Sealed by Available Sealants: Expected From Tests to be Made
1	Phenol		*
2	Methyl Alcohol	x	
3, 8, 14, 18	Insecticides, Rodenticides	x(DDT)	x(others)
4	Acrylonitrile		
5	Chlorosulfonic Acid+		
6	Benzene	x	
9	Phosphorus Pentasulfide+		
10	Styrene		x
11	Acetone Cyanohydrin	x	
13	Nonyl Phenol	x	
15	Isoprene		x
16	Xylene		x
17	Nitrophenol	x	

x = Polyurethane or Epoxy Sealants
* = Butyl, Polysulfide and Neoprene Rubber Sealants
+ = Not sealed with available sealants

drum full of water. The rubber elasticity of the swelled Neoprene allowed the pressure of the water to produce normal stresses that contributed to expansion of the mass on the inside of the container. The material still behaved as a viscous liquid and so slowly extruded through the hole; a permanent seal is required to prevent the leak from redeveloping.

Another two-inch diameter hole was permanently sealed by first applying a plug of the 3M polysulfide rubber putty, followed by a patch of the Sea Goin' Poxy Putty on a strip of nylon cloth which encircled the container. The cloth girdle held the epoxy in place while it hardened, and in about two hours the entire seal was hard enough to allow any usual handling of the 5-gallon container.

The Instant Foams supplied by Monsanto were contained in pressurized cylinders. Upon opening a valve, solid foam is delivered. These materials may be useful in sealing leaks of compatible hazardous chemicals by forming a mechanical plug.

Additional evaluation tests and scale-up investigations were made with some of the most promising sealants. These included investigation of the effects of: barrier type (e.g., patch, outside plug, plug expanded outside and inside), thickness of barrier, speed of application, type of applicator, technique of application, and temporary support during the curing stage. The primary emphasis of the scale-up work has been to increase the hole sizes and hydraulic heads against which leaks can be plugged.

Earlier testing with various available plastic systems indicated the need for having a flexible laboratory mixing/delivery system in order to perform effective evaluation tests. No available mixing system was found which could perform the necessary functions, so a system was designed and constructed. It uses an in-line "static" mixer and can meter the components to supply various mixtures over a range of flowrates. It has been used for tests with urethane foams, and can be modified to permit its use with more viscous systems, such as some of the epoxy formulations.

A promising technique for sealing large holes with urethane foam against appreciable hydrostatic heads is to expand it both inside and outside the hole. This results in a structural bridge. It is important to apply the foam at a point in its curing cycle where it will adhere to the container surface. This requires some type of temporary support. This has led to the concept of either a special applicator design (large cross-section, long residence time), or a two-stage application technique. In the latter concept, the foam is mixed externally and allowed to cure for a few seconds until it reaches the right stage of tackiness. It is then applied to the leak with some device which provides temporary support for an additional few seconds until sufficient rigidity has developed. An important key to successful operation with this concept is that the applicator be designed in such a way as to provide some compression of the tacky foam while forcing it through the leaking hole. Thus, the foam will expand on the other side of the hole to provide a structural bridge, but have sufficient internal cohesion while expanding to avoid being washed away.

A variety of applicator concepts can be envisioned for practical usage: an extremely simple one has been tested with considerable success. A large suction cup ("plumber's helper") is filled with foam and allowed to set for a few seconds until the proper tackiness is reached. The cup is then placed against the leaking stream, and some of the foam is forced through the hole with the plunger. The sides of the cup provide enough restraint so that the necessary compression of the foam cells can be achieved, resulting in expansion on the inside of the hole. It is not necessary that the cup exactly conform to the surface of the container. This technique has been used successfully to seal a 1-1/2-inch hole in a 55-gallon drum with three feet of head. Tests with larger holes and greater liquid heads are scheduled. The hydraulic force of the stream from such a hole would immediately wash away any sealant material if it were not applied with a special application system and in sufficient quantities to bridge the hole.

CONCLUSIONS

The feasibility of this concept for plugging leaking chemical containers has been demonstrated, including sealing of many different hazardous chemicals and application to leaks both underwater and in air. Successful scale-up tests have been made with containers of up to 55-gallon capacity. As a consequence of the progress realized to date, it is predicted that a practical and useful system, embodying this concept, can be developed.

ACKNOWLEDGEMENT

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IDENTIFICATION OF SPILLED HAZARDOUS CHEMICALS*

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To shut off sources of spills, clean up spilled materials, identify polluters and make numerous decisions in handling hazardous chemical spills it is helpful, if not necessary, to identify the chemicals involved. Often spilled chemicals are hazardous at concentrations below 1 part per million in the receiving waters. For example, Endrin, a chlorinated pesticide, kills fish at a concentration of 0.0002 parts per million. Automated, remote control instruments cannot identify chemicals in water at sub-parts-per-million levels, therefore samples of contaminated water must be analyzed in the laboratory.

It is important that the analytical chemist work closely with the field investigator in laying out a sampling program and analyzing data. Any information that may help point to the source of a spill, identify samples that are expected to contain high (or low) concentrations of the spilled chemical, eliminate specific chemicals from consideration or point to more likely specific chemicals should be thoroughly considered. Often chemical analysis is required merely to confirm identity if use is made of all other information available.

An analysis of the information in Table I illustrates the importance of considering results of chemical analysis and other information together. These data were obtained during the investigation of a fish kill in the Tombigbee River. Samples were collected almost simultaneously so that stream flow during sampling can be ignored. An agricultural chemical manufacturing plant is located just upstream from sample 2. Dead fish were observed in the areas from which samples 4 through 8 were collected.

A list of products manufactured at the plant indicated that three pesticides, Diazinon, Atrazine and Chlorobenzilate, were being produced at the time the first dead fish were observed. With this information the choice of compounds whose concentration should be measured was reduced several thousand fold to just three.

A study of the concentration profile for each of these three chemicals indicates

- a sudden release was made of all three of them simultaneously,
- the dead fish were found in the area of the river where the concentration of each of them was highest, and
- samples had been taken soon enough after the release of material to show that it was released above river mile 58.5 and below river mile 64.0. Sample #2 is essentially the "treated" effluent of the plant before dilution by the receiving stream.

Operators of the plant were somewhat perplexed that the evidence indicated one of their products killed fish since the "treated" effluent was indicated nontoxic by bioassay tests at the time the materials were released. Further analysis of the table, and consideration of the toxicities to fish for each of the three pesticides pointed out the "spilled" chemical. The ratios of Diazinon to Atrazine and to Chlorobenzilate in the samples from the fish kill area are much higher than these ratios are in sample 2, the effluent that was sampled for bioassay. Diazinon was also the only one of the three chemicals that exceeded acute toxicity levels (The 96-hour TLm values for Diazinon, Atrazine and Chlorobenzilate

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*The mention of trade names or commercial products in this report does not constitute endorsement by the Environmental Protection Agency.

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TABLE I

Concentration of Pesticides in River Water Samples

Sample #	River Mile	Diazinon ppb	Atrazine ppb	Chlorobenzilate ppb
1	64.0	<0.1	0.17	< 0.3
2				
2(A)	60.8	168	1900	184
3	58.5	18	28	0.8
4*	56.0	42	62	1.3
5*	55.3	139	120	3.8
6*	54.6	98	110	3.7
7*	54.6	198	130	4.2
8*	54.0	110	69	2.5
9	53.3	6.2	6	0.3
10	51.7	0.8	37	< 0.3
11	48.8	0.3	51	< 0.4

A Effluent

* Fish Kill Area

are 90 ppb, 9300 ppb and 670 ppb respectively for Bluegill.)

Faced with this information the plant manager made a thorough inspection of his operation. He found that a process line in his Diazinon plant had not been removed as it should have been, and it was possible for a plant operator to turn a valve allowing Diazinon waste to bypass the treatment facility and the bioassay-test sampling points. Inadvertent opening of this valve had caused the spill.

The concentrations of the pesticides were determined by comparing the gas chromatogram of each compound to that of a standard of known concentration of the compound. Compounds were identified by comparing their gas chromatographic retention times to those of standards of known composition. Because of the consistency of data from this investigation it may have been possible to prosecute the polluter with no further confirmation of the presence of Diazinon. The identification of Diazinon was confirmed, however, by comparing the mass spectrum of the material whose GC retention time was the same as that for Diazinon with the mass spectrum of Diazinon. Figure 1 demonstrates that the material was indeed Diazinon.

Identification of Organic Chemicals

Until a few years ago the identification of specific organic chemicals in rivers or lakes was considered impractical for investigation of water pollution incidents because it required so much time and effort. The application of gas chromatography to pesticide analysis demonstrated that low concentrations of some organic compounds could be measured rapidly in water. Unfortunately the GC retention time is not adequate identification when thousands of possible compounds must be considered.

Development of mass spectrometers with fast scan times made possible obtaining a mass spectrum of any material that could be separated by gas chromatography. Acceptable spectra can be obtained with as little as 10^{-8} grams of compounds injected into a gas chromatograph interfaced with a mass spectrometer. By extracting and concentrating the organic compounds from one liter of water, a mass spectrum can be obtained for most compounds present in concentrations from 10 to 100 parts per trillion (nanograms per liter) or greater.

A typical procedure involves extracting most organic materials from the water into an organic solvent such as chloroform or hexane. Extractions are usually made after adjusting the pH of the water to several different values so that more compounds can be extracted. This adjustment also results in some separation of compounds. The organic extracts are concentrated in volume to approximately 50 microliters (if ultimate sensitivity is required), and then 1 to 10 microliters are injected into the gas chromatograph. The gas chromatograph separates the components of the mixture with respect to time and feeds them to the mass spectrometer.

The quadrupole mass spectrometer, Figure 2, ionizes the neutral molecules of the vaporized sample in the ionizer by electron bombardment. In the process of ionization, molecular bonds are broken, producing fragments of varying mass-to-charge ratios (m/e), which comprise the "cracking pattern" for the compound. The quadrupole mass "filter" separates fragmented ions with respect to their m/e. Most ions entering the quadrupole field take an unstable exponential trajectory and strike the

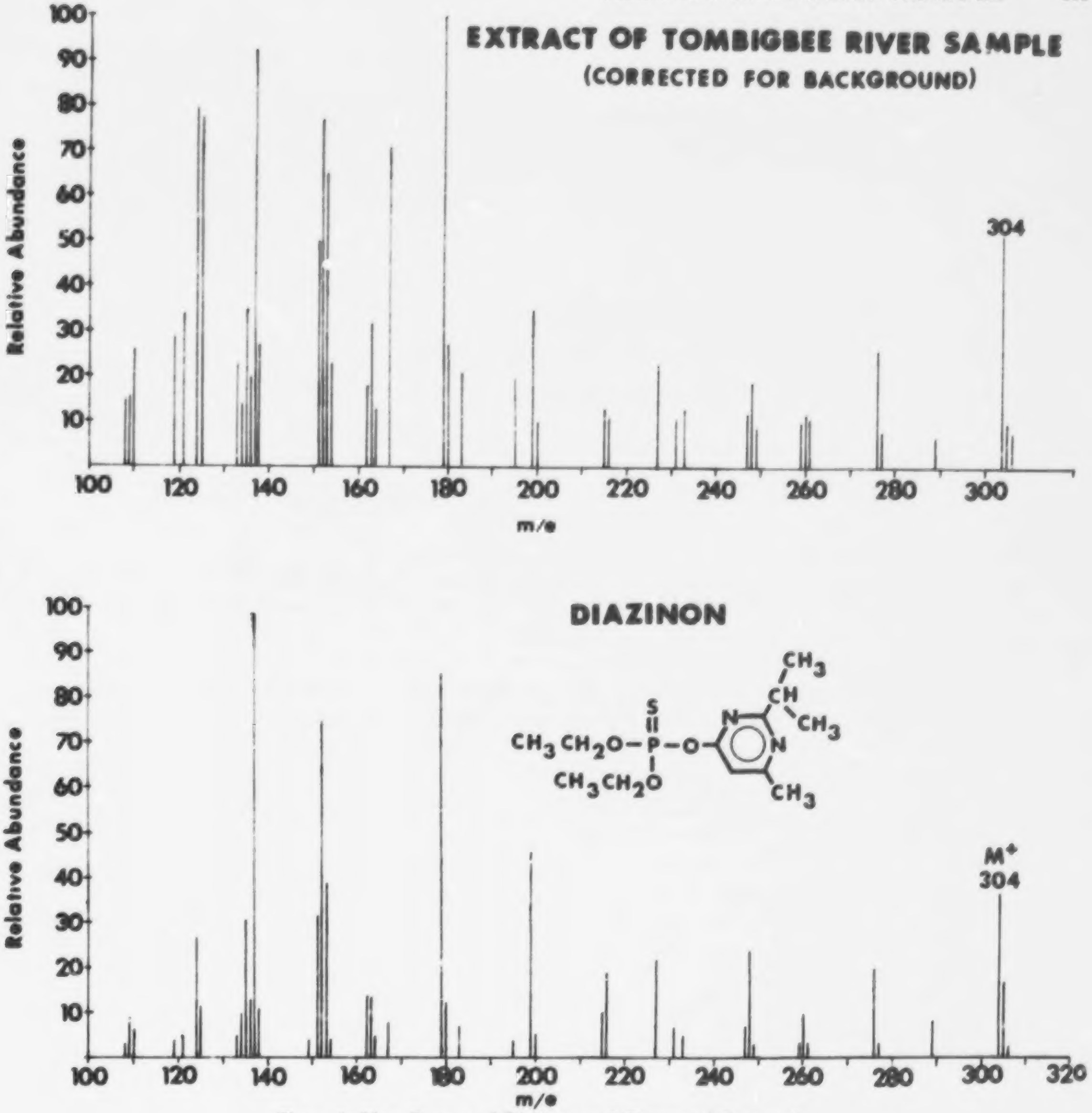

Figure 1: Mass Spectra of Diazinon and Compound Separated from River Water

rods. For one value of m/e (at a given time) the ions take a bounded trajectory, allowing them to pass through the mass filter and strike the electron multiplier detector. The detector signal is amplified and displayed on an appropriate device or recorded on magnetic tape. As the voltage is scanned with respect to time, varying species of m/e are allowed through the mass filter.

The mass spectrum of a compound isolated from a fish kill in a TVA lake is compared to that of phenyl mercuric chloride in Figure 3. In this case the selection of phenyl mercuric chloride was reasonably straightforward from the mass spectrum of the unknown. Because there are five naturally occurring isotopes of mercury at greater than six percent isotopic abundance, molecular fragments containing mercury are easily recognized in this spectrum. Notice the clusters of five ions around m/e 314 (phenyl mercuric chloride ion), m/e 279 (phenyl mercury ion), and m/e 202 (elemental mercury ion).

The compound that was identified as phenyl mercuric chloride was isolated by TVA scientist and identified at the Southeast Water Laboratory. Phenyl mercuric chloride is a decomposition product of phenyl mercuric acetate. Though the exact source of phenyl mercuric chloride was not confirmed, many steel drums that formerly contained phenyl mercuric acetate were used as floats for piers in the lake.

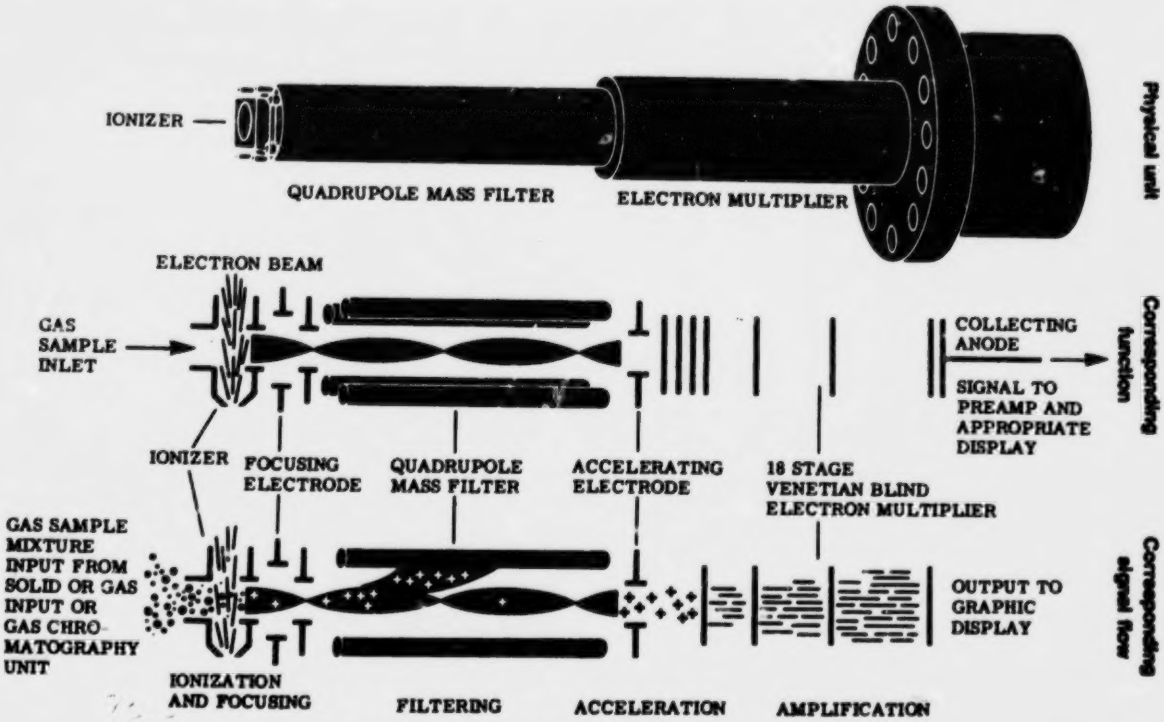

Figure 2: Separation of Masses by Quadrupole Mass Spectrometer (By Permission from Finnigan Corporation)

Since their removal, large fish kills, which occurred almost annually in Boone Lake, have not recurred.

Interpretation of mass spectra is often complex and tedious. Computerized spectral matching shows promise of simplifying this task significantly, and a project is now underway at the Southeast Water Laboratory to develop a computer search program for identifying organic compounds from their mass spectra. As the program is refined a separate file of hazardous organic chemicals will be compiled to speed the identification of a spilled hazardous chemical.

The mass spectrometer is not the only tool that is helpful in identifying organic compounds, but it is the only one capable of making a spectrum "on the fly" for a 10 ng effluent from a GC. As of January 1972, EPA had 10 mass spectrometers in use for identifying organic pollutants in water and several more will be added before July 1972.

Compounds that cannot be identified by their mass spectra alone must be subjected to further analysis. The infrared spectrum is quite definitive for functional groups, and empirical comparisons of infrared spectra can also be made. With Fourier transform techniques it is possible to obtain an infrared spectrum with 10 ng of pure material, but the sample must be collected and mounted in a KBr pellet to attain this sensitivity. Nuclear magnetic resonance spectrometry is sometimes required to elucidate the structure of an unknown organic compound, but a milligram of pure compound is needed for such measurements.

To confirm the identity of an unknown organic compound its spectrum should be compared with a reference spectrum of the compound it is believed to be. It may be necessary to synthesize the reference compound if it is not commercially available and its spectrum is not on file.

The time required for identifying organic compounds by spectral analysis other than computerized empirical matching programs makes compilation of comprehensive and reliable spectral libraries for water pollutants imperative.

Table II lists organic compounds that were identified in a solids waste dump near the Missouri River, and Table III compares compounds extracted from an industrial effluent and those in foam on the Gulf of Mexico twenty-five miles away. As spectra of compounds such as these are added to computer search files and separations techniques are improved, the time required to identify organic pollutants will become shorter and shorter.

Elemental Analysis

Most soluble inorganic compounds become ionized in aqueous solution to the extent that their original molecular form is no longer of significance.

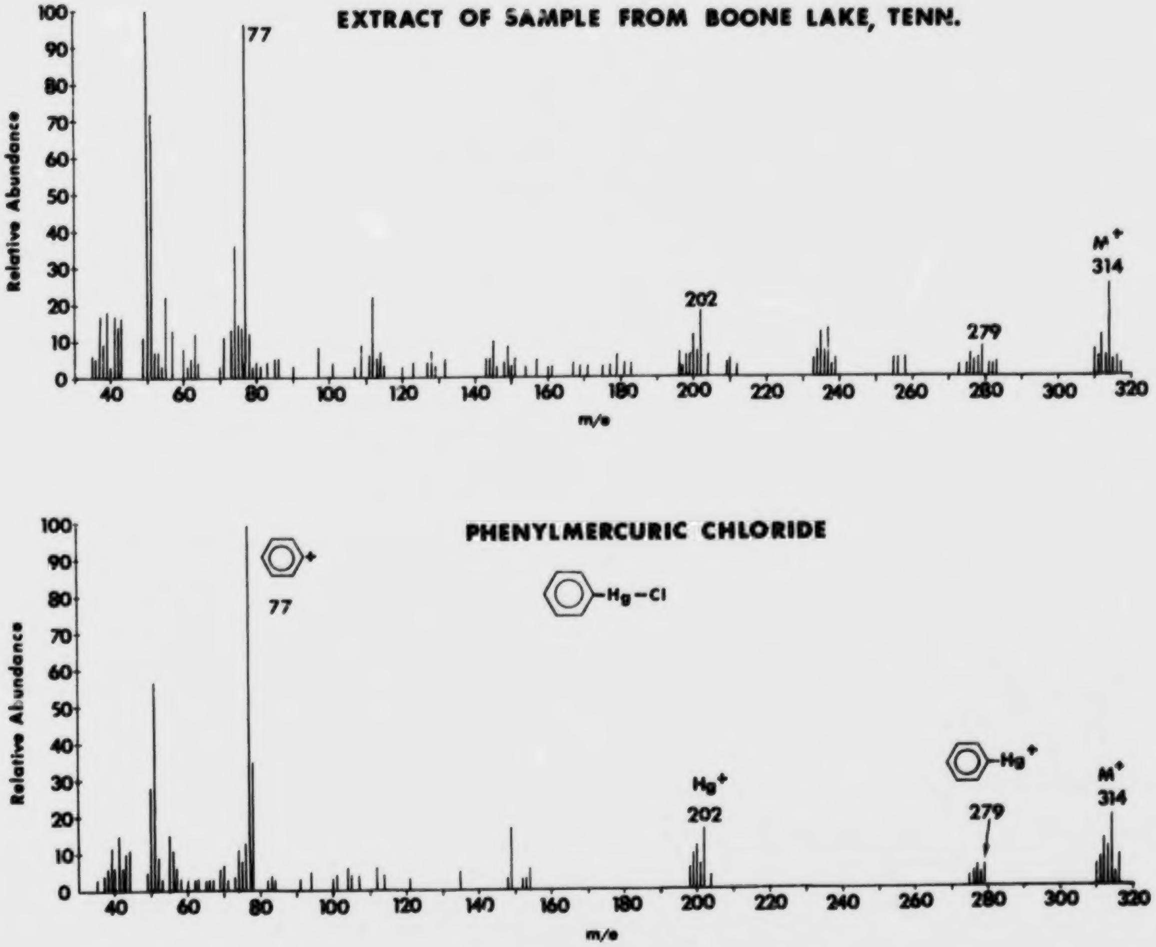

Figure 3: Mass Spectra of Phenyl Mercuric Chloride and Compound from Lake Water

This is particularly true when the anion in the original compound is one of the more prevalent anions in natural water, such as chloride, sulfate, nitrate or carbonate, as is often the case. Therefore, identifying spilled inorganic chemicals can be greatly enhanced by elemental analysis, especially when differences in elemental composition of samples from the spill can be compared with those from the surrounding waters.

Almost half of the ninety-two naturally occurring chemical elements could cause problems if in solution at an undesirable concentration, so a complete elemental analysis is extremely helpful in assessing the significance of spilled inorganic compounds. The concentration of the other elements present may be helpful as a "fingerprint" in locating the source of the spill. Therefore, qualitative and quantitative knowledge of the chemical elements in samples should be obtained as thoroughly as practical unless sufficient information is available to limit concern to a few chemical elements.

Several analytical techniques permit the analyst to scan qualitatively for the elements. The spark source mass spectrometer considers all elements except the inert gases and hydrogen. It has relatively uniform sensitivity for all elements. Lower level of detection for all elements in a 50 m*l* sample is about 10 parts per trillion. Only neutron activation analysis is competitive in sensitivity for a large number of elements. Detection levels with neutron activation vary widely. Emission spectroscopy is useful for some elements, and it is more rapid than mass spectrometry, but sensitivity is poor. X-ray fluorescence may prove to be a good elemental scanning technique if proton induced excitation is used to increase sensitivity.

TABLE II

Compounds in Solids Waste Dump

Phenol
o-Cresol
p-Cresol
p-Cresol
2,6-Ditertiarybatyl-p-cresol
Benzothiazole
1-Methyl-4-ethylbenzene

n-alkane (18 carbons)
Diethyl phthlate

1-Indanone
Methyl biphenyl
Methyl naphthlene
Dimethyl naphthlene

TABLE III

Resin Acids in Foam and Industrial Effluent

Foam in Gulf	Mill Effluent
Pimaric acid	Pimaric ACID
Isopimaric acid	Isopimaric acid
Hydroabietic acid	Hydroabietic acid
Palmitic acid	Palmitic acid
Resin Acid, MW 312	Resin Acid, MW 312
Resin Acid, MW 318	Resin Acid, MW 318
Unknown Compound, MW 264	Unknown Compound, MW 264
Resin Acid, MW 314	

At the Southeast Water Laboratory we are assessing the applicability of spark source mass spectrometry for elemental scanning of water samples.

In the spark source mass spectrometer the sample is vaporized by a high radio-frequency spark. Every compound is completely fragmented into its chemical elements. The vaporized elements are then ionized, accelerated and separated according to their mass to charge ratios as they pass through a magnetic field. The masses are scanned in a manner similar to quadrupole mass scanning. The principal shortcoming of the spark source mass spectrometer is the time required for data analysis, but hopefully this will be

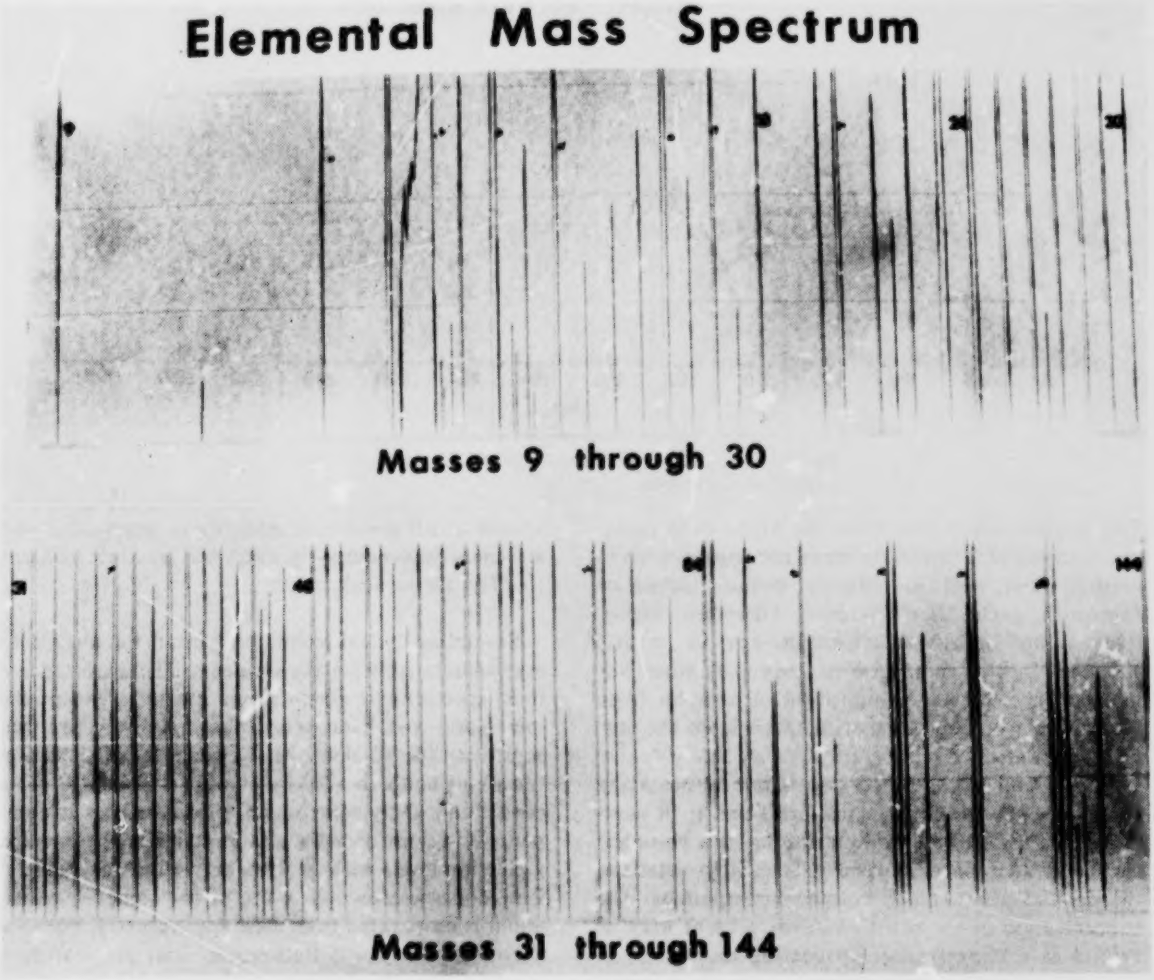

Figure 4: Spark Source Mass Spectrum

alleviated with a computerized data analysis system. If the data analysis program currently being evaluated at SEWL can be sufficiently "debugged," one can obtain a computer print-out of the concentration of every chemical element present in a water sample above a concentration of 10 parts per trillion within two hours after receipt of the sample in the laboratory

Figure 4 shows the mass spectrum from mass 9 to 144 for an effluent from a metal plating plant. Intensities of signals for masses above 144 were insignificant. Attenuation was reduced to detect trace elements, but all signal intensities, including those that exceeded full scale, were recorded by the computer. Figure 5 shows the recorded masses and signal intensities. The machine-computed elemental composition is displayed in Figure 6. One part per million computed by the data analysis system (with a yttrium reference) is equivalent to approximately 0.1 ppm in the effluent.

Because of advances in the capability to identify chemicals in water, there is great promise that the analyst and the field investigator, working closely, will sharply reduce the number of spills whose sources remain undetected. A corresponding reduction in the total number of spills should soon follow. At the Southeast Water Laboratory, the Water Contaminants Characterization Research Program is continuing to evaluate and develop better and faster means for identifying chemical pollutants with a goal of reducing chemical spills to an insignificant source of water pollution.

```
AECPH2R3

 PK.  NORM.    ACC.          PK.  NORM.    ACC.          PK.  NORM.    ACC.
 NO.  INTY.    MASS          NO.  INTY.    MASS          NO.  INTY.    MASS

   1    331   146.42          45    432   54.00           89      2   21.96
   2    585   145.24          46    599   53.03           90     64   21.50
   3   1430   144.01 R        47   1251   52.00           91    646   21.01
   4     96   137.47          48    711   50.04           92      2   20.53
   5      2   135.09          49    966   49.03           93   1651   20.00
   6    190   133.16          50   1315   48.00 R         94    637   19.51
   7    740   132.00          51    396   46.03           95    754   18.03
   8   1268   130.94          52    336   45.04           96   1185   17.02
   9   1035   120.87          53    255   44.51           97      3   16.53
  10    924   120.01 R        54   1113   44.02           98    123   16.50
  11    191   113.45          55    524   43.03           99   1992   16.00 R
  12    146   110.60          56    584   42.04          100      2   15.75
  13      2   110.50          57    953   41.02          101    325   15.51
  14    650   109.61          58   1612   39.99          102      3   15.05
  15    702   108.65          59   1603   38.99          103    101   15.02
  16      2   106.07          60      2   38.86          104      2   14.58
  17     70    98.22          61    388   38.07          105   1563   14.05
  18    298    97.17          62      3   37.15          106      3   13.67
  19    989    96.01 R        63   1229   37.02          107    319   13.55
  20     87    92.48          64   1698   36.00 R        108      2   13.19
  21     81    92.06          65    876   35.02          109   2543   13.06
  22    882    88.97          66   1314   33.99          110      3   13.00
  23    141    88.00          67    882   33.01          111      2   12.95
  24    267    86.10          68    164   32.50          112      2   12.87
  25   1021    85.07          69   1697   32.00          113      4   12.61
  26   1074    84.05          70    345   31.51          114    675   12.56
  27    297    80.08          71      2   31.46          115      4   12.36
  28    451    76.03          72    904   31.02          116      2   12.30
  29    148    74.09          73    783   30.03          117     11   12.19
  30    764    73.04          74   1028   29.03          118  10000   12.00 R
  31   1022    72.00 R        75   1444   28.01          119     23   11.72
  32     72    69.02          76      3   27.54          120      3   11.72
  33    807    68.00          77   1095   27.02          121      2   11.68
  34    505    66.00          78      7   26.51          122      2   11.67
  35    754    64.99          79   1267   26.03          123      2   11.64
  36    872    64.00          80      2   25.90          124   1855   11.59
  37    905    62.98          81   1537   25.03          125      2   11.43
  38     92    61.97          82      3   24.95          126      2   11.35
  39    995    61.03          83   1943   24.00          127    338   11.10
  40   1252    60.00 R        84      3   23.90          128      2   10.91
  41      2    58.97          85   2920   22.99 R        129    762   10.75
  42    954    58.00          86      2   22.82          130      2   10.59
  43    956    56.02          87      3   22.75          131   1043    8.10
  44    259    55.02          88    849   22.00          132     75    7.76

INTERPRET ?  :Y
```

Figure 5: Computer Print-Out of Corrected Masses and Normalized Intensities from Spark Source Mass Spectrum

```
MASS  ELEMENT         PPM        ++?   CONFIRM   CHECK     COMPLEX
                     ATOMIC      +++?  ISOTOPES  OVERLAP   IONS


 133  CESIUM             .43     NO      -
 121  ANTIMONY          4.22     NO      NO
  89  YTTRIUM      STANDARD
  88  STRONTIUM          .38     NO     YES
  85  RUBIDIUM          3.24     NO      NO
  80  SELENIUM          1.34     NO      NO
  72  GERMANIUM         8.57     NO     YES
  69  GALLIUM            .28     NO      NO
  66  ZINC              4.12     NO     YES                C4N (   66)
                                                           C4O (   68)
                                                           C4O (   64)
                                                           C4C (   64)
  63  COPPER            3.07     2+     YES                C4OH(   65)
  58  NICKEL            3.24     NO     YES                C4N (   62)
                                                           C4C (   60)
  59  COBALT             .00     NO      -
  56  IRON              2.38     NO     YES                C3OH(   56)
  55  MANGANESE          .58     2+      -                 C3O (   55)
  52  CHROMIUM          3.40     2+      NO                C3O (   52)
                                                           C4  (   52)
                                                           C3OH(   53)
                                                           C3N (   53)
                                                           C4H (   53)
  48  TITANIUM          4.17     NO      NO     144(   48)
                                                           C3C (   48)
                                                           C4  (   48)
  45  SCANDIUM           .76     NO      -
  40  CALCIUM           3.65     2+     YES                C2O (   40)
                                                           C2N (   40)
                                                           C3H (   40)
                                                           C2OH(   43)
  39  POTASSIUM         3.99     2+      NO                C3  (   39)
                                                           C2OH(   41)
  35  CHLORINE          2.58     NO      NO      74(   37)
                                                           C3H (   37)
  34  SULPHUR          71.53     2+      NO
  31  PHOSPHORUS        2.05     2+      -
  28  SILICON           3.60     2+      NO                CO (   28)
                                                           COH(   29)
                                                           CO (   29)
                                                           COH(   30)
  27  ALUMINIUM         2.48     2+      -                 CN (   27)
                                                           C2H (   27)
  24  MAGNESIUM         5.72     2+      NO                CC (   24)
                                                           C2  (   24)
                                                           C2H (   25)
                                                           CC (   25)
                                                           CN (   26)
                                                           C2  (   26)
  23  SODIUM            6.62     2+      -
  16  OXYGEN            4.51     NO      -
```

Figure 6: Computer Print-Out of Analyzed Data from Spark Source Mass Spectrometer

METHODS FOR THE DETECTION AND MARKING OF SPILLED HAZARDOUS MATERIAL

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Cornell Aeronautical Laboratory, Inc.

ABSTRACT

This paper deals with the early detection of hazardous spills and post-spill monitoring of their extent. For early detection, reliable, automatic sensors, single or in arrays, could be emplaced where spills may be anticipated. After detection, monitoring using colorimetry, smell and electrical conductivity appear most appropriate for untrained personnel. Among applicable methods for detecting pollutants in water, catalytic combustion sensors have been found useful for sensing volatile organics; electrical conductivity is effective in detecting ionic solutes; and pH as well as certain specific ion probes are useful for indicating acids, bases, and metallic pollutants. Less volatile organics can be sensed with a multicolor transmissometer now in development. A variety of other compounds, especially heavy metal pollutants, can be detected by a colorimeter with greatly reduced sensitivity to turbidity and fouling. To monitor pollutants after a spill, colorimetric indicators, smell, and conductivity appear most suitable. A set of colorimetric indicators is being selected, and an extremely simple conductance meter was developed. Sensitivity of these detectors and the sense of smell in gauging selected pollutants is being measured in the laboratory and in natural water bodies.

Detection of Hazardous Spills

Hazardous chemical spills should be detected quickly, both to limit damage to biotae and to facilitate treatment which is most effective when the spill is still concentrated. Although many spills cannot be anticipated, in certain probable locations such as industrial rivers, detector arrays could be effective at a reasonable cost. Individual detectors should react to a wide spectrum of possible pollutants; for example, pH indicators, which are responsive to acids, bases, and solutions of liquid ammonia. Under the sponsorship of the Environmental Protection Agency (EPA), Cornell Aeronautical Laboratory, Inc. (CAL) is conducting a study to select sensors that are commercially available or can be quickly developed, and that are suitable for unattended, long-term use where a spill may reasonably be expected. Much of the effort centers on the selection of apparatus that will resist deterioration in the environment of industrial sewers and rivers.

Among applicable methods for detecting pollutants in water, electrical conductivity is effective in detecting the presence of ionic solutes; pH and certain other specific ion probes are useful for indicating the presence of acids, bases, and metallic pollutants; and catalytic combustion sensors have been found useful for sensing volatile organics. Less volatile organics can be detected with a multicolor transmissometer currently being developed. A variety of other compounds, especially heavy metal pollutants, are detectable with a "cyclic colorimeter" that uses modulation of indicator injection to greatly reduce sensitivity to turbidity and fouling.

Vapor Sensors

Several commercial catalytic combustion sensors or vapor sniffers have been evaluated for the detection of various volatile materials. Figure 1 shows their performance in detecting pollutants in water by sampling the vapors above their aqueous solutions at room temperature. The chemicals chosen represent broad classes of pollutants. The concen-

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CHEMICAL	CRITICAL* CONCENTRATION (ppm)	DETECTION LIMIT (ppm)	DETECTION LIMIT / CRITICAL CONCENTRATION
AMMONIUM HYDROXIDE	5.0	310	62
CHLORIDE	0.03	3300**	10^5
METHANOL	250	700	2.8
PHENOL	0.1	8000	10^5
ACRYLONITRILE	15	45	3
ACETONE CYANOHYDRIN	1-100	2×10^4	10^4

* CONCENTRATION AT WHICH BEHAVIORAL EFFECTS ARE OBSERVABLE.

**RESPONSE OF OPPOSITE POLARITY (DEPRESSION OF COMBUSTION).

Figure 1: "Sniffer" Response to Representative Chemicals

tration of each chemical which produces a noticeable effect on fish in an acute dose is listed for comparison. It is obvious that many hazardous materials (those similar to methanol or acrylonitrile) can presently be detected at a useful level, (about three times as high as that noticeable to fish), but in some cases greater sensitivity is desired and a number of approaches to attain it are being investigated.

Electro Chemical Measurements

The conductivity of water is traditionally used as a measure of purity for distilled and deionized water. Since the conductivity of fresh water in most streams and lakes is fairly low, a sudden increase in conductivity indicates the presence of an ionic solute, probably a pollutant. Conductivity is usually measured with alternating current to avoid interference from a plethora of ionic reactions which occur when direct current is applied to electrodes in water. The laboratory approach uses platinum electrodes, alternating current at a few hundred hertz, and circuitry to match one's budget. For field use, a more rugged, telemetering device is necessary. We have investigated two varieites of conductance meters.

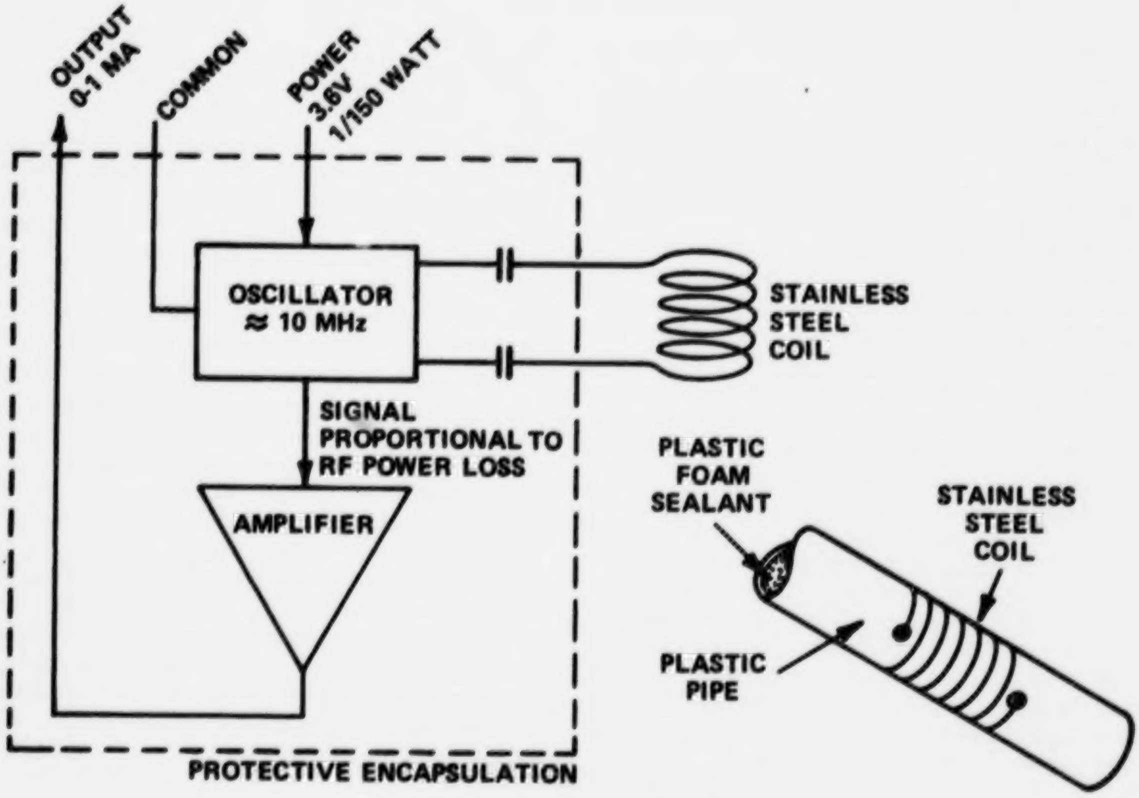


Figure 2: Radio-Frequency Oil Sensor

The first (shown in Figure 2) was developed for use in sewers, where it discriminates between sewage and oil accumulations in traps.[1] It is extremely rugged, as attested by its continuous use for several years in an inverted syphon in Buffalo, New York. Conductivity is measured by the load presented to a small radio frequency oscillator immersed in the fluid.[2] Regrettably, it is most sensitive to variations of conductivity in a range typical for oil pollutants and very pure water. An attempt to extend its range to the less pure water in streams failed. In Figure 3, the impedance of one centimeter

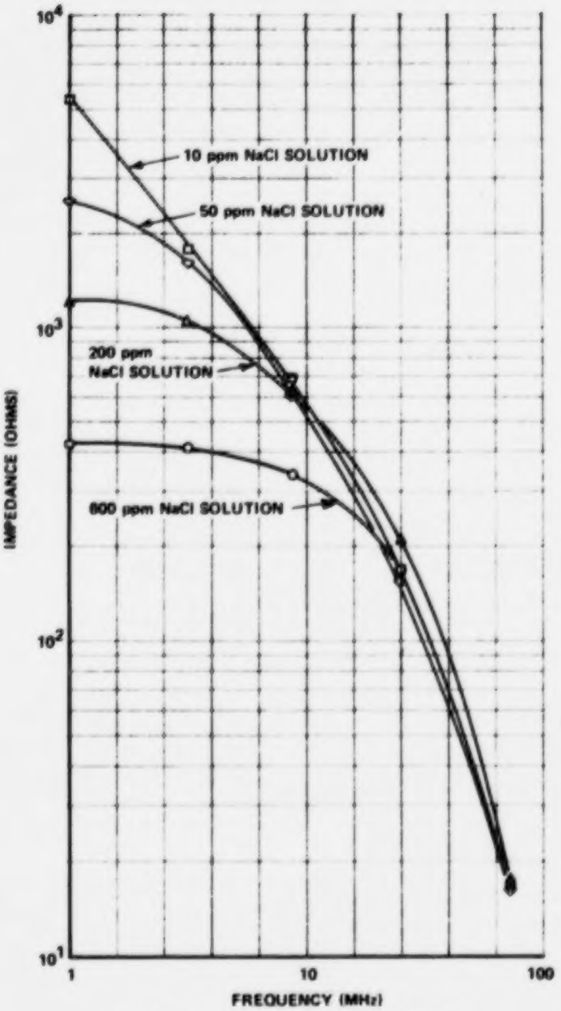


Figure 3: Solution Impedance vs Frequency

cubes of solutions is shown as a function of frequency. It is apparent that at radio frequencies, the impedance is lower and the concentrations of interest are compressed into a narrow range of measured impedances.

Several commercial instruments can measure audio-frequency conductivity. We have built a simple, inexpensive, telemetering device using this principle which is shown in Figure 4. It consists of a voltage controlled oscillator (VCO) operating between 200 and 3000 hertz. The control voltage is derived from a rectifier that measures the output of an AC ohm meter. This ohm meter measures the resistance between two stainless steel probes immersed in water, and is excited by the output of the VCO. The various functions of the conductivity meter, including FM telemetry, can thus be performed by one transistor with a power input of a few milliwatts, provided by a 3-volt battery. The FM output is transformer-coupled to avoid ground loops, and may be recorded on tape and demodulated with a simple read-out device, or used as a modulating signal for radio telemetry. Figure 5 is the record of a ferrous sulfate spill as it passed the detector of an early breadboard version of this meter during a spill simulation. Fairly high noise was recorded from flutter and wow in the inexpensive tape recorder used for this test.

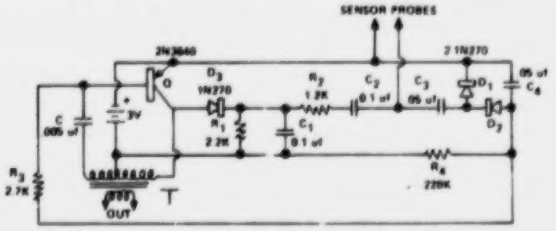


Figure 4: Audio-Frequency Conductance Meter

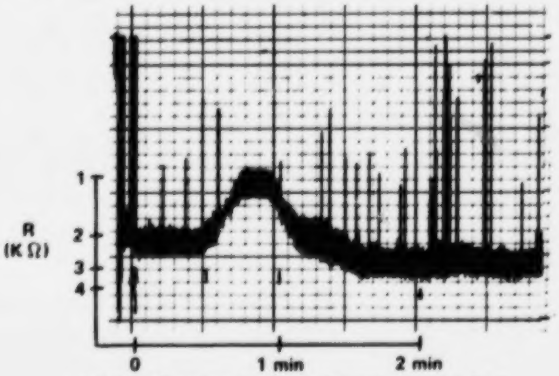


Figure 5: Conductivity Meter Record—Colden Spill

Electrodes for pH measurement have recently graduated from the laboratory to on-line control capability, and there is little doubt that they will find wide application in pollution monitoring. They have already been used in oceanography, where compensation for high ambient pressure is necessary.[3] We have used specific ion electrodes, which are quite similar, to trace the concentration of sulfide and bivalent metal ions in spill simulations. These electrodes appear to have some sensitivity to flow, pressure, and ground loops, but are otherwise quite effective. Figure 6 shows profiles of sulfide ion taken at four stations along a stream during sulfide precipitation of the ferrous sulfate spill referred to earlier. At that time we could not connect the output of several specific ion probes to one recorder because of ground loop problems. The readings were made visually from the meter, and later plotted versus elapsed time. All four curves were made with two instruments; one was moved to a point ahead of the spill to start a new sequence while the other was measuring.

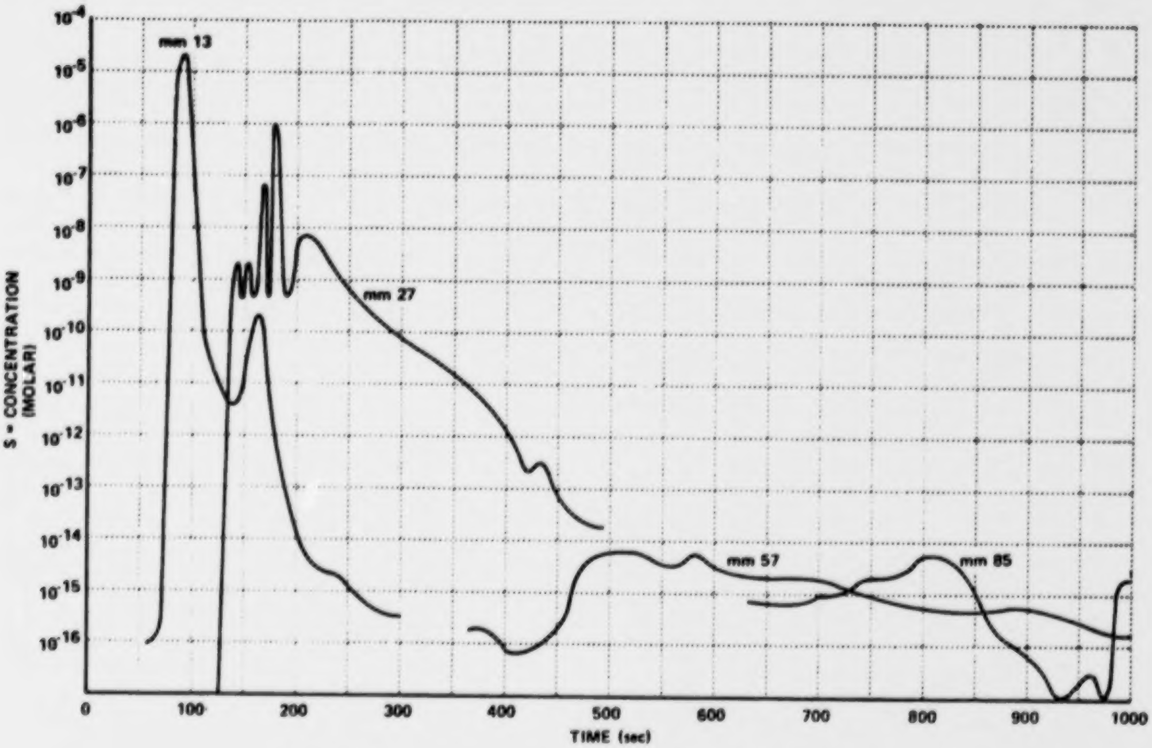


Figure 6: Sulfide Ion Concentration vs Time at Several Sampling Points

Spectroscopic Measurements

Some time ago, we evaluated a two color transmissometer for detecting oil in sewers.[1] It operated in the near-ultraviolet and red visible regions of the spectrum. Since several other hazardous chemicals show absorption in the near and far ultra-violet, we conducted further tests of transmissometers with a view toward developing an unattended pollutant sensor. The problems with this approach are fairly obvious: one cannot expect precision optics to perform well for any duration under water. The two-color transmissometer was operated for about six weeks in a Buffalo sewer. By using two colors, it was possible to detect fouling. The oils to be detected are fairly opaque in the near ultraviolet and at least translucent for red light. If the red light signal that was periodically radio-telemetered to our laboratory disappeared, we could assume that the device, shown in Figure 7, was fouled. To our surprise, it was fouled by scale from hard water, after about one week. After cleaning with dilute hydrochloric acid it remained useable for over one month, when the UV emission from the argon lamp became too weak for further use. During this time, only one oil spill was detected. From the calibration of the instrument, we estimated a concentration of tens of parts per million; a sample taken shortly after detection contained hundreds of parts per million of oil.

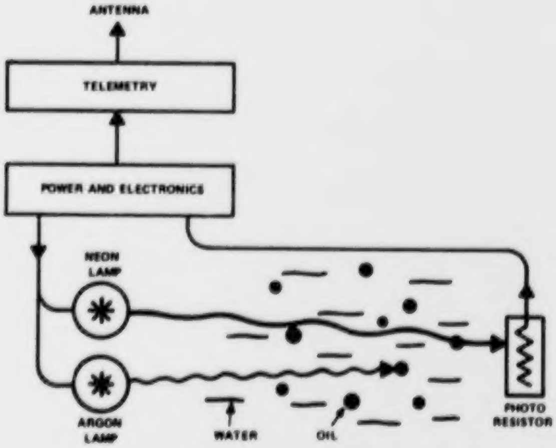


Figure 7: Near-Ultraviolet Oil Sensor

Improvements in calibration and resistance to fouling are clearly needed. We are therefore looking for a design that keeps precision optics out of the water. Figure 8 shows an arrangement with a diffuse reflector under water and all other optics above the surface. The cone shape of the reflector should enable it to shed sediment through the hole at the bot-

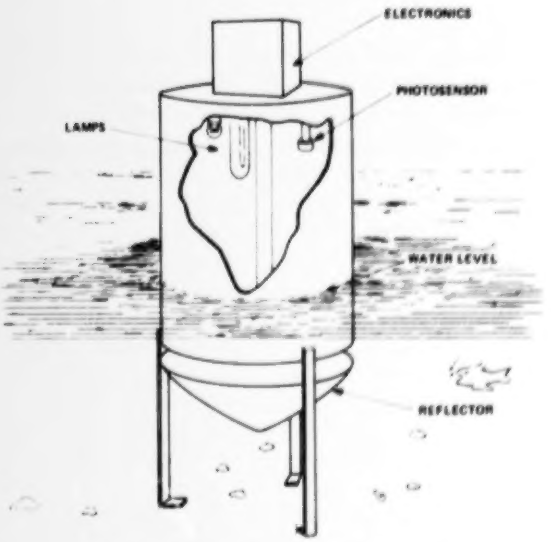


Figure 8: Multispectral Transmissometer

tom. The argon and neon lamps used in earlier designs have been replaced with germicidal, fluorescent black-light, and incadescent lamps, emitting at 254, 360, and about 600 nanometer wavelengths. Unfortunately the data for the evaluation of this design were not complete at the time of this writing.

Single color transmissometers for on-line process control are commercially available, including at least two operating at 254 nanometers for detecting oil in boiler water and possibly tanker ballast.[4] Fouling is not expected in boiler water. When pumping ballast the operation is intermittent; rust scale from the tanker holds can be removed by flushing with acid. In this general class of instruments, there is also a surface-reflection sensor for oil slicks.[5] We have found the wave suppressor configuration used with this sensor to be very effective and have incorporated a similar feature into our instrument buoy, shown in Figure 9.

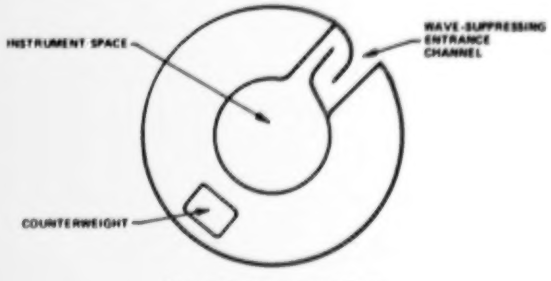


Figure 9: Instrument Buoy

Many chemicals can be detected with colorimetric indicators and detectors. To circumvent fouling of optical components in an unattended instrument we modulated the indicator injection and read the difference in absorption with and without the indicator. A cross-section of the apparatus is shown in Figure 10. The indicator is permitted to drop through an orifice. Since the timing of the modulation by this mechanism is quite variable, the system is synchronized by detecting the drop with a photocell in the vertical branch of the colorimeter. Another photocell monitors absorption in the process stream. Its output signals are processed to derive a measure of the change in coloration after addition of the indicator, even in the presence of background color. Immediately after the indicator drop hits the process stream, the signal is integrated with a positive sign for the duration of the slug of colored water which is shown passing through the discharge tube of a breadboard apparatus in Figure 11. After the slug is past, the sign of the integrand is reversed for an equal interval. In the absence of an indication, no total change in integrator output is noted. If there is more absorption of light during the slug treated with indicator, there is a net charge on the integrator at the end of the cycle. At this time, the integrator voltage is transferred to a sample-and-hold circuit to simplify read-out, and the signal integrator is reset. Figure 12 shows the response of the instrument to a heavy metal ion, with sodium sulfide as an indicator. Addition of a dye to the process stream to a level that reduced transmission by a factor of ten changed the response to the heavy

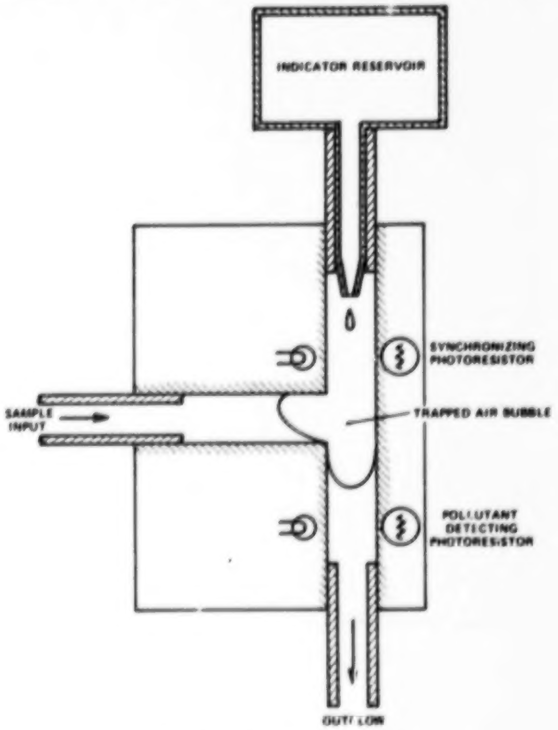

INDICATOR RESERVOIR
SYNCHRONIZING PHOTORESISTOR
SAMPLE INPUT
TRAPPED AIR BUBBLE
POLLUTANT DETECTING PHOTORESISTOR
OUTFLOW

Figure 10: Cyclic Colorimeter

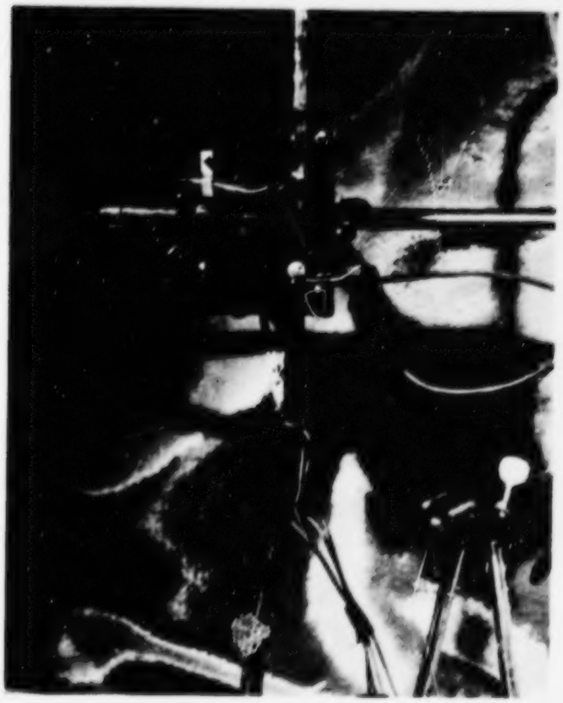


Figure 11: Breadboard of Cyclic Colorimeter

metal very little, as shown in the lower part of Figure 12. Figure 13 shows the calibration curve of the colorimeter with and without this quantity of dye.

The cyclic colorimeter is now being evaluated to test its sensitivity to chemicals difficult to detect by conductivity, pH, vapor sniffing, and multicolor transmissometers. The colorimeter effectively detects many heavy metal ions which form sulfide precipitates as shown on a periodic chart, Figure 14, where we have shown only those elements against which the technique was tested. Some difficulty is encountered with certain combinations of pollutants and indicators because the color change reaction is too slow to be detected in a sample stream running at a useful velocity. If one compensates for a slow reaction by measuring far downstream, turbulence in the stream causes mixing of the indicator slug with the reference slug.

The instruments discussed so far have either exhibited resistance to deterioration or have a good chance to do so. They are, of course, less sensitive than the best laboratory methods, such as atomic absorption spectroscopy. But these instruments are useful for initial detection of a spill. Their outputs, properly thresholded, could trigger sampling de-

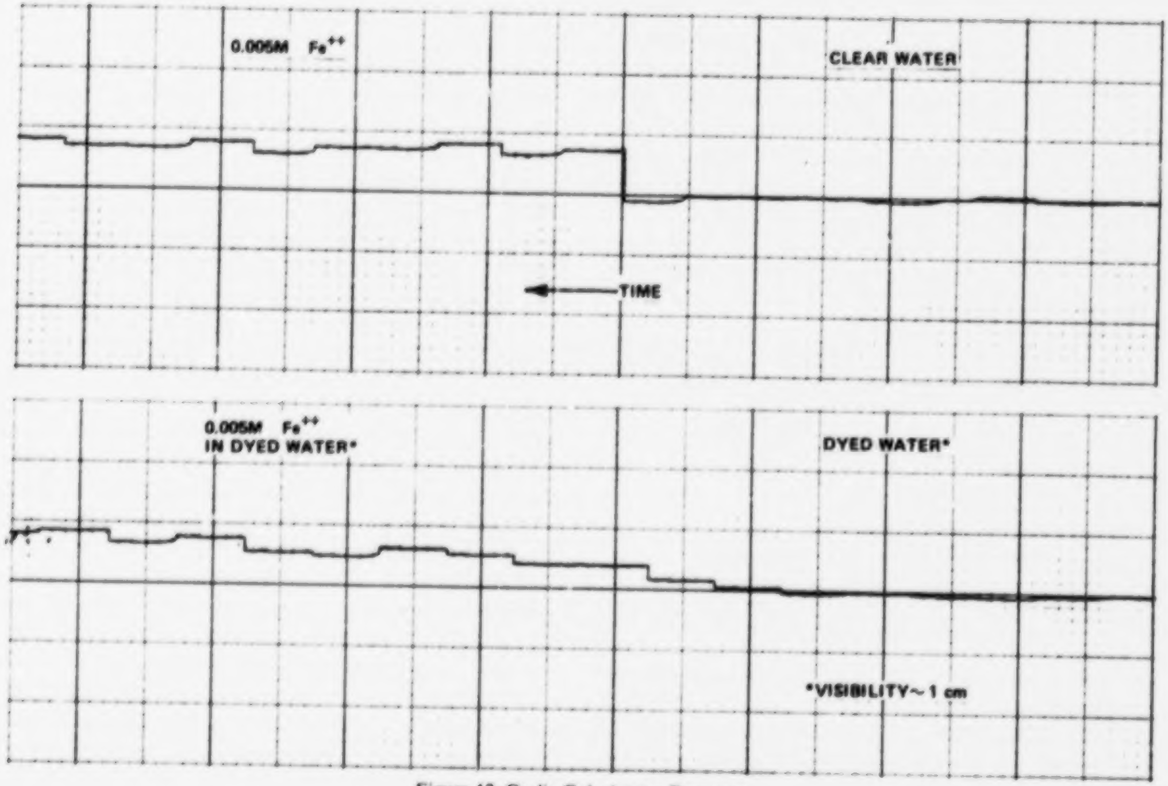


Figure 12: Cyclic Colorimeter Response

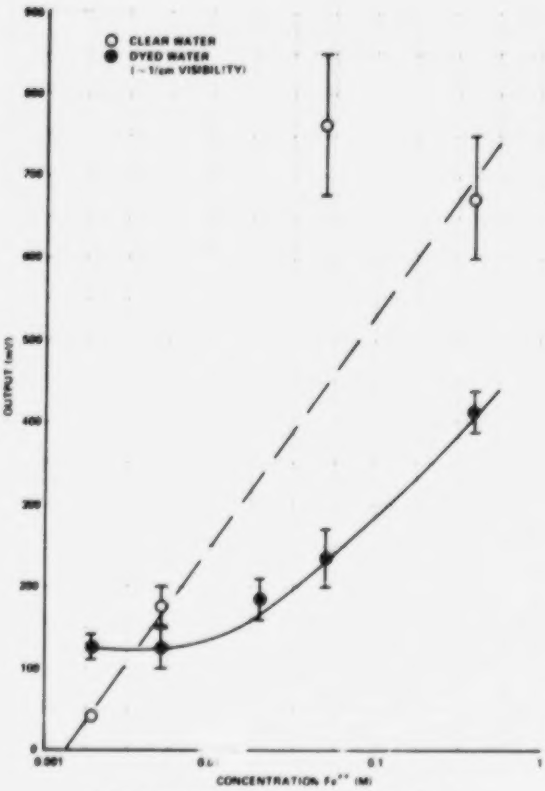


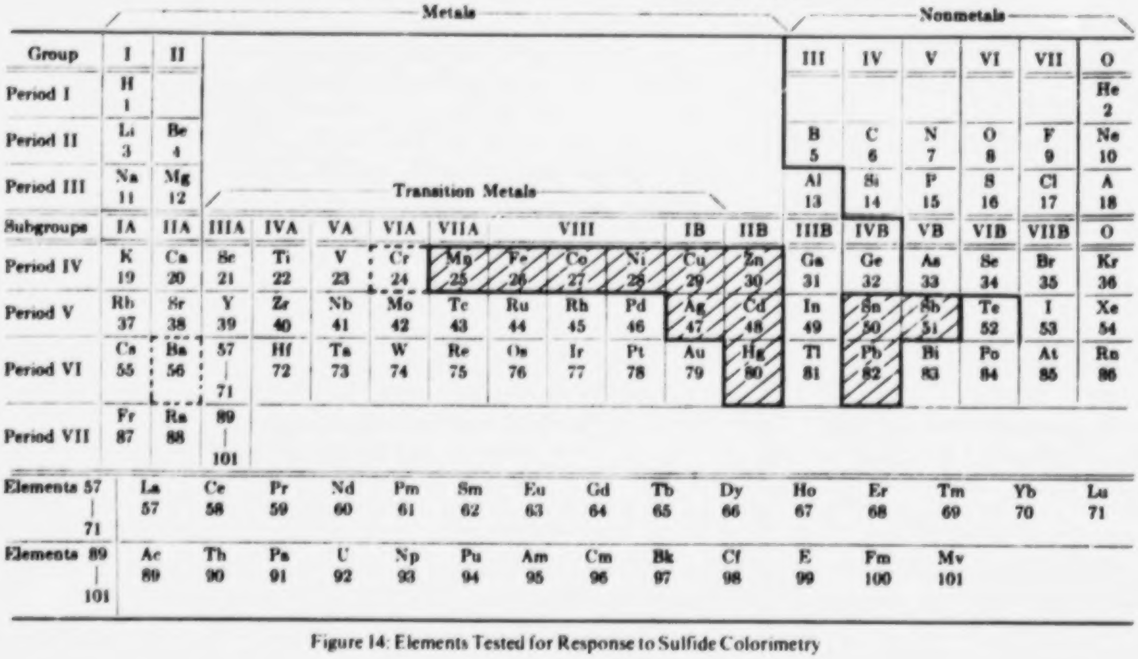
Figure 13: Cyclic Colorimeter Calibration

vices, thereby significantly reducing the number of samples to be analyzed later. In this form, these instruments are useful for tracing a spill and monitoring its progress.

Monitoring Existing Spills

For most spill situations, one cannot expect to have a full complement of fieldable, analytical instruments and the trained personnel to operate them. It, therefore, seemed useful to select a group of less sophisticated indicators that could be effectively used by personnel coping with hazardous spills. Many of these people will not have been trained in chemistry. The indicators must be simple to use and fairly foolproof. They should cover at least the most common and hazardous substances, and they should be very inexpensive to permit widespread distribution. In selecting indicators, we reviewed a history of hazardous spills compiled by the Environmental Protection Agency, as well as a report on potential hazards compiled by Battelle under EPA contract.[6] It became apparent that the likely spill materials can be detected by one of the following characteristics:

1. pH
2. Smell
3. Conductivity
4. Sulfide or Chromate Precipitation


Metals
Nonmetals
Transition Metals

Group	I	II											III	IV	V	VI	VII	O
Period I	H 1																	He 2
Period II	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Period III	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	A 18
Subgroups	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	O
Period IV	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Period V	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Period VI	Cs 55	Ba 56	57 │ 71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Period VII	Fr 87	Ra 88	89 │ 101															

Elements 57 │ 71	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Elements 89 │ 101	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	E 99	Fm 100	Mv 101		

Figure 14: Elements Tested for Response to Sulfide Colorimetry

Identification by these characteristics is clearly difficult and should properly be left to a chemist. This does not say that treatment cannot be initiated with the limited information derived from these tests. Frequently one has an estimate of the quantity of material lost. For example, many times no more than a few pounds of a poisonous heavy metal compound are spilled. If the addition of a sulfide precipitation indicator shows such a compound to be present, one can safely apply a small amount of treatment. If one still discovers the metal ion downstream, one can continue with this approach until a chemist and a hydrologist can estimate the exact quantity of residual treatment needed. The treatment of an acid or base spill is even simpler. One simply adds enough neutralizing agent to bring pH into the range from six to eight. If one considers the complexity of first aid procedures mastered by many public employees, it seems likely that fairly simple treatment procedures can be carried out as described above.

Many citizens are already familiar with pH measurement through their experience with swimming pools. Bromothymol Blue, the most common indicator, has a very narrow range of sensitivity, and we have sought one with a more useful range. Such a pH indicator, superior to several universal paper indicators in readability and reproducibility, was described by Yamada.[7] It contains four indicators and goes through the colors of the spectrum in the pH range from 4 to 10 (Figure 15). Furthermore, it remains red for pH less than 4 and violet for pH greater than 10. The change in color with one pH unit, with the possible exception of the change from pH 9 to 10, is sufficiently clear to override the masking effects of even fairly murky water.

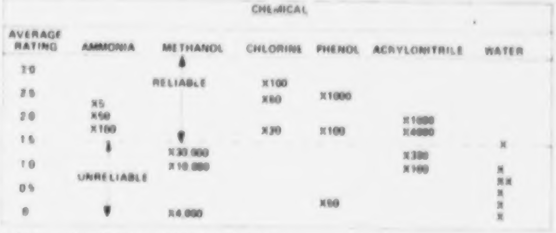
5 mg	**THYMOL BLUE**
12.5 mg	**METHYL RED**
60 mg	**BROMTHYMOL BLUE**
100 mg	**PHENOLPHTHALEIN**

(+100 ml H_2O, 100 ml EtOH
TITRATE TO GREEN WITH NaOH)

pH	COLOR
4	RED
5	ORANGE
6	YELLOW
7	GREEN
8	BLUE
9	INDIGO
10	VIOLET

Figure 15: pH Indicator

A group of psychologists at Cornell Aeronautical Laboratory conducted tests on the sensitivity of olfactory detection of a number of chemicals in aqueous solution. Small covered jars with coded labels were each filled to 75% capacity with either distilled water or a measured concentration of acrylonitrile, ammonia, chlorine, methanol, or phenol in distilled water. Each jar was shaken briefly and then uncapped and presented to the subject, who rated the intensity of the odor on a scale from 0 to 3. Six subjects were presented with various solutions in water of acrylonitrile, phenol, and with distilled water alone. Six other subjects were presented with various solutions of chlorine, ammonia, methanol and with distilled water. Each subject smelled the vapors rising from each solution in water or the water alone. When the concentrations of the acrylonitrile solution in water was 1000 ppm, phenol 100 ppm, chlorine 20 ppm and ammonia 5 ppm, smelling of the vapors emanating from each of these solutions led to fairly reliable detection as shown in Figure 16. For lesser concentrations of these chemicals and for all concentrations of methanol up to and including 30,000 ppm, the ratings overlap those given to distilled water. These tests will be repeated using natural waters from creeks, rivers, and lakes to obtain a more realistic estimate of olfactory sensitivity to pollutants.



CONCENTRATIONS ARE IN PARTS PER MILLION

Figure 16: Smell Intensities

The same group found that sulfide precipitation can be used to detect a considerable variety of heavy metals, and that precipitation of barium chromate, by using either barium chloride or potassium dischromate as an indicator, serves to identify chromate ion and barium. A simple kit, based on these three indicators, has been developed to permit unskilled personnel to identify heavy metal spills. The kit contains three color coded bottles, each containing a premeasured amount of one of the indicators. To identify a spill, one need only fill each bottle with the suspect water, recap and shake the bottles, and note the bottle and color of any precipitate which forms. Appropriate treatment of the spill can be initiated, if necessary, merely on the basis of which bottle contains the precipitate, or the results of the test can be called to a regional headquarters for further instructions. The sensitivity of these tests to heavy metal pollutants and the range over which the indications are semi-quantitative are shown in Figure 17.

The ultimate goal of this phase of the study is a kit that would likely include, (in addition to the heavy metal indicator kit) a pH indicator, several sample bottles to help identify chemicals by smell,

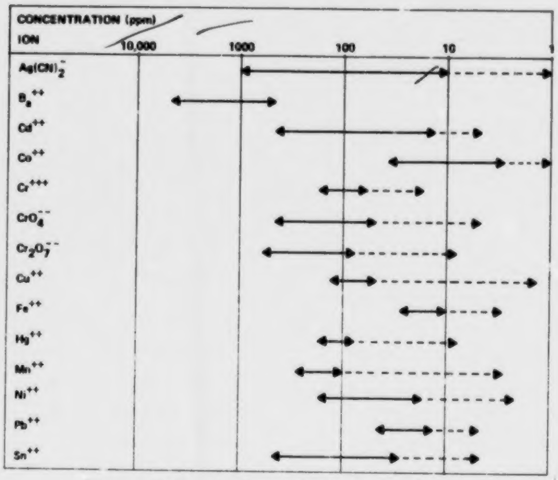


Figure 17: Colorimetric Discrimination Range

and a very simple conductivity probe, probably a modification of the telemetering probe described earlier. This kit might usefully be augmented by one or several of the sensitive indicator kits for mercury and lead recently marketed and by an oil sampling kit developed by Dr. Robert Baier at Cornell Aeronautical Laboratory.

In some spill situations, one may be able to add an identifying dye to the spilled chemical before or shortly after it enters a waterway. As little dye as possible should be used to minimize cost and harmful side effects of the dye, while assuring detection of the spill boundary at a significant pollutant concentration. Two fluorescent dyes, Rhodamine B and Disodium Fluorescein, are suitable as tracers. They can be detected visually at dilutions of about fifty parts per billion, and at lesser concentrations with fluorimeters. To apply one of these dyes to a chemical that should be detected at a level of one part per million, one pound of dye would be needed for every twenty pounds of pollutant. If several barrels of pollutant are spilled, the cost of the tracer is probably acceptable; if tank car quantities are spilled it may not be. Some potential pollutants interfere with the access of ultraviolet rays to the dye or with its fluorescence. We have observed that silver salts and molybdates suppress the activity of Disodium Fluorescein (see Figure 18), and we are testing for other interferences. Oil films are almost sure to be a problem.

SALT	DISODIUM FLUORESCEIN	RHODAMINE B
AMMONIUM MOLYBDATE	MODERATE	MODERATE
ZINC CHLORIDE	MODERATE	MODERATE
SILVER NITRATE	COMPLETE–ARMY DRAB GREEN COLORATION	NONE
SODIUM CHROMATE	MODERATE	MODERATE
SODIUM ARSENATE	NONE	NONE
CADMIUM CHLORIDE	MODERATE	NONE
MANGANOUS SULFATE	MODERATE	NONE
COBALT CHLORIDE	COMPLETE–BUFF COLORATION	MODERATE
NICKELOUS SULFATE	MODERATE	MODERATE
BARIUM ACETATE	NONE	SLIGHT

Figure 18: Attenuation of Dye Fluorescence by Selected Heavy Metal Salts

Detection or tracing of an extensive list of chemicals was investigated in our recent studies. Although a wide range of pollutants is satisfactorily covered, sensitivity should be improved by one or two orders of magnitude for other substances.

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A RAPID DETECTION SYSTEM FOR ORGANOPHOSPHATES IN WATER

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ABSTRACT

Spills of hazardous materials into rivers, streams or lakes could result in the poisoning of individuals who consume water from municipal water supplies. There is now a need to detect these hazardous spills in time to close off the intake valves to these water supplies before any human or animal toxic effects are produced. A Continuous Aqueous Monitor (CAM-1) has now been designed and fabricated which has the potential capability of warning water-plant operators should hazardous quantities of organophosphate insecticides suddenly appear in the raw water supplies. CAM-1 uses immobilized cholinesterase for the collection of organophosphates and other cholinesterase for the collection of organophosphates and other cholinesterase inhibitors from the water supplies. The activity of the immobilized enzyme is determined automatically in an electrochemical cell. By alternately using the immobilized enzyme to sample the water and then assaying the enzyme for its residual activity during a 3-minute detection and warning cycle, it is possible, with the aid of a mini-computer, to sound an alarm in three minutes or less with the appearance of sub-toxic levels of the organophosphates in the raw water supplies. The unit which has been developed is undergoing extensive tests to determine its potential for use in the Water Monitoring Network.

INTRODUCTION

As further restrictions are placed on the use of chlorinated hydrocarbons as insecticides, it is inevitable that the use or organophosphate insecticides will continue to increase. Many environmentalists believe that organophosphates are the lesser of two evils, since most of them decompose in soil or water without the build-up of toxic residues. Further, there are few reports showing the build-up of the organophosphates in the body fat of animals high in the food chain. In spite of the good qualities of the organophosphates we must not over-look the fact that under certain conditions some of them persist in the environment for prolonged periods of time. For example, Thoman and Nicholson[1] (1963) reported that organophosphate wastes containing parathion discharged into a river in the southeastern part of the United States caused an extensive fish kill for 25 miles and affected fish in a reservoir 100 miles downstream.

An important review of the recovery, separation and identification of organic pesticides from natural and potable waters has been published by Faust and Suffet.[2] The following information on the persistance of organophosphates has been adapted from the work of Muhlmann and Schrader:[3]

From this table it is clear that both water temperature and pH are important factors in the stability of the organic phosphate insecticides in water. It will be observed that some of these compounds persist at hazardous levels in water supplies for months or even years if the water is cool and the pH is on the neutral or acid side. In waters of high alkalinity the persistence of the organophosphates is much reduced, but may, at low temperatures, have half-lives measured in days and weeks instead of months and years. Since some organophosphates persist for long periods of time under conditions common in streams, lakes and

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TABLE I

Half-Life of Some Organophosphate Insecticides in Water at pH 1-5[3]

Temp. (°C)	Paraoxon	Parathion	Dipterex	DDVP	Methyl Parathion
			Days		
10	1200	3000	2400	240	760
20	320	690	526	61.5	175
30	93	180	140	17.3	45
50	9.6	15	10.7	0.66	4.0
70	1.2	1.65	1.13	0.164	0.47
			Hours		
70					
pH 3	23.0	21.0	33.0	3.4	11.2
pH 5	24.4	19.5	15.3	2.8	10.7
pH 7	11.5	7.8	0.7	0.45	6.9
pH 9	2.1	2.7	0.1	—	1.5

ponds, it is imperative that we have the capability of detecting hazardous spills of these materials into water supplies prior to their ingestion by fish, wildlife and humans.

A number of analytical methods for the detection and identification of these compounds have been reported. Because these compounds are toxic at such low levels, it is usually necessary to collect the organophosphate on a column of activated charcoal to get a large enough sample to permit gas chromatography, mass spectrometry, etc.

For example, Davis and Malaney[4] collected the acetylcholinesterase inhibitors from water supplies using a charcoal column; chloroform was then used to extract the organophosphates from the column before measuring the enzyme inhibition capacity of the chloroform extracts.

Guilbault *et al.*[5] reported an electrochemical assay procedure for organophosphate insecticides based on their inhibition of cholinesterase and its conversion of a substrate to a hydrolysis product which depolarized platinum electrodes to which a constant current was applied. Builbault *et al.*[6] also showed cholinesterases from different insect species were inhibited to different degrees by different organophosphates, and that both sensitivity and selectivity could be used to achieve trace analyses of pesticides by enzymatic methods.

In his discussion of equipment for monitoring pollutants in water, Porterfield[7] enumerated some of the common water pollutants for which there was no monitoring equipment available. He implied that the lack of standards for organophosphates in water was tied to a lack of suitable monitoring equipment. Some investigators have felt that perhaps the important thing for them to know was whether there were *any* toxic substances in the water supplies rather than just the concentration of one or more specific insecticides. To accomplish this goal, Cairns *et al.*[8] set up equipment for continuous monitoring of the activity of aquatic life; in one system he monitored the heart rate and breathing rate of bluegill sunfish for the detection of sublethal concentrations of zinc ions and other toxicants. In spite of their success, a non-living toxic hazard monitoring system could have many advantages.

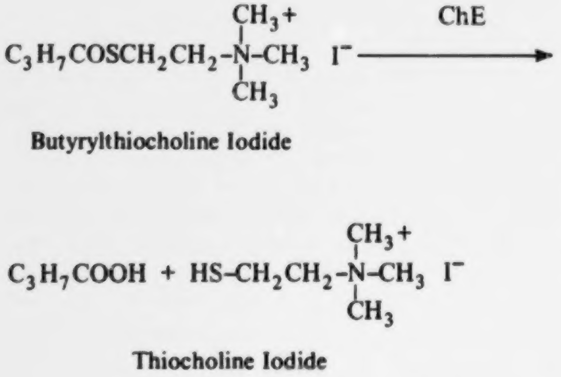
In trying to develop a system which could be used to monitor water supplies for the presence of toxic substances, we were reminded of a statement in the report of the National Technical Advisory Committee:[9] "The most important mechanism of toxic action is thought to be the poisoning of enzyme systems." Although we realize that this statement may be an oversimplification of toxic phenomena, at the same time, we are firmly convinced that enzymes offer a great potential for the detection of toxic substances. It was for this reason we proposed to the Federal Water Quality Office that (1) they sponsor a search for a group of enzymes which could be used in the detection of toxic substances in water supplies and (2) that a water monitoring apparatus based upon the use of immobilized cholinesterase as the sensor be constructed for the purpose of detecting those toxic substances which inhibit cholinesterase, e.g., organophosphate insecticides, some carbamate insecticides and some heavy metals.

Investigation by Bauman *et al.*[10] had shown that cholinesterase immobilized by starch gel on the surface of open-pore urethane foam could be used in an electrochemical cell for the continuous monitoring of air for the presence of cholinesterase inhibitors. In this system the air being sampled and a solution of substrate for the enzyme were pumped simultaneously and continuously through the immobilized enzyme product; activity of the enzyme was then monitored continuously by passing an electric current through platinum electrodes in contact with the immobilized enzyme product and observing changes in the electrode potentials. Further explanation of this detection principle is described in this report.

Detection Principle and Its Adaptation to Water Monitoring

The detection principle used in the monitoring of water for the presence of toxic substance in water can be divided into the following parts: (1) the collection of the enzyme inhibitors on immobilized cholinesterase, (2) the chemical reaction of immobilized cholinesterase with its substrate, and (3) the electrochemical monitoring of substrate hydrolysis products. The mechanisms by which enzyme inhibitors block the activities of enzymes have been extensively investigated. In most, if not all, of the known examples of enzyme inhibition, the inhibitor becomes attached either reversibly or non-reversibly to the active sites of the enzyme and blocks the substrate from these sites. Many of the organophosphates are known to be non-competitive inhibitors of cholinesterase. For this reason, immobilized cholinesterase is able to capture and collect pure or mixed organophosphates from very dilute aqueous solutions and produce a response even when very low levels of inhibitors were sampled. We think that non-competitive inhibitors may also be collected by immobilized enzymes, but higher concentrations of them would be required for them to be detected by a system such as that described in this report.

The chemical reaction which we have chosen for use with the immobilized enzyme is shown by the following equation:



$$C_3H_7COSCH_2CH_2\text{-}\overset{CH_3+}{\underset{CH_3}{N}}\text{-}CH_3\ I^- \xrightarrow{ChE}$$

Butyrylthiocholine Iodide

$$C_3H_7COOH + HS\text{-}CH_2CH_2\text{-}\overset{CH_3+}{\underset{CH_3}{N}}\text{-}CH_3\ I^-$$

Thiocholine Iodide

In this reaction a thioester is cleaved by the enzyme cholinesterase to give a product with a free thiol group, thiocholine iodide. Under the influence of an electric current the free thiol group is converted to the disulfide:

$$2\,RSH - 2\,e \xrightarrow{\text{anode reaction}} RS\text{-}SR + 2\,[H]$$

Without going deeply into the theory, it is sufficient to say that when an electric current is passed through two platinum electrodes in the presence of unhydrolyzed substrate, a voltage of about 400 mV is produced (i.e., under the conditions we employed using an applied current of about 2.0 μA). On the other hand, if the enzyme is active, it will hydrolyze the substrate to liberate some of the thiol and produce an electrode potential about 200 mV lower than the potential observed when only the unhydrolyzed substrate is present. Thus by passing substrate through the electrochemical cell and observing the potentials, it is possible to tell whether the enzyme has or has not been inactivated.

The design of an electrochemical cell adapted for water monitoring of enzyme inhibitors is shown in Figure 1. From the drawing it will be noted that an enzyme immobilized enzyme pad is located between two perforated platinum electrodes. The constant current is supplied by a battery (e.g., 6V) or other source in series with a resistance (e.g., 4 megohms), so that a current of about 2 μA flows through the circuit. A high impedance voltmeter or electrometer is used to monitor the voltage. During the water pumping part of the cycle only water is passed through the enzyme pad, but during the substrate pumping cycle both air and substrate solution are pumped through the cell. The air flow is needed to push most of the water from the cell and reduce the dilution of the substrate solution; also the air helps to control the amount of liquid in the enzyme pad during the voltage measurements.

In the previous descriptions we have referred briefly to the detection cycle we adopted in order to make the enzyme system suitable for water monitoring. Originally, we had hoped that it would be possible to sample water and monitor the activity of the enzyme pad continuously. We chose the intermittent sampling system for two reasons: (1) if water and substrate solution were pumped simultaneously through the enzyme pad, excessively large quantities of substrate would be required to maintain the correct concentration of the substrate for the enzyme reaction, and (2) similarly, large quantities of buffer would be required to maintain the proper pH of the substrate in the presence of large volumes of raw water. We have, therefore, devised a two cycle detection process which consists of (1) an inhibitor col-

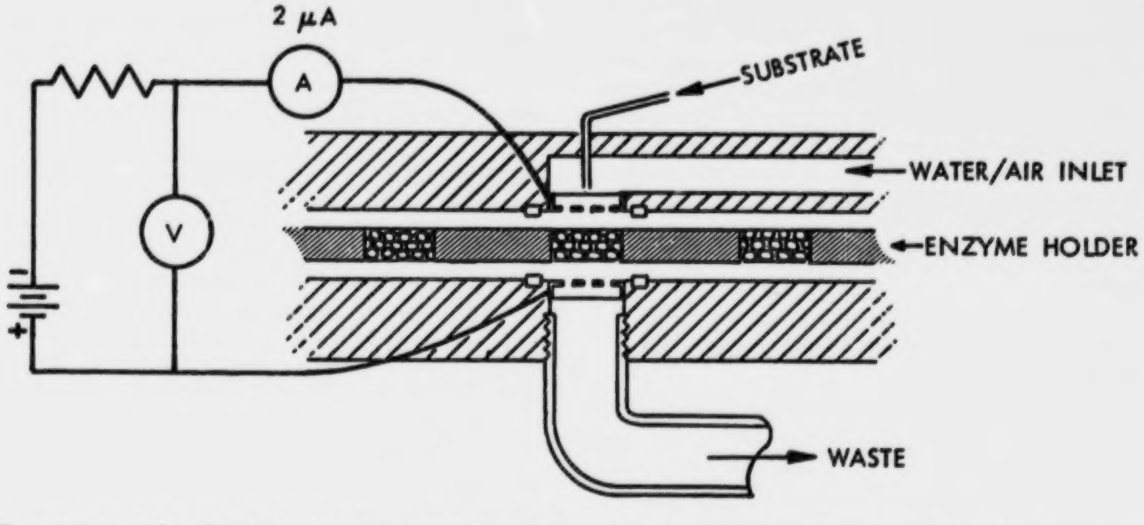


Figure 1: Cross section of Electrochemical Enzyme Cell Showing Connections for the Constant Current Supply and the Electrometer

lection step lasting 2 minutes and an enzyme activity monitoring step lasting 1 minute. During the inhibitor-collection part of the cycle, water is sampled at approximately 1000 ml/min for 2 minutes; the excess water is then blown out of the cell with an air pump. During the enzyme-monitoring part of the cycle the substrate solution is pumped through the cell, a constant current is applied to the electrodes, and the cell potential is measured and compared with the cell potential from the preceding cycle. An increase in cell voltage between cycles is the signal used to determine whether inhibitors were present during the inhibitor-collection cycle.

An important consideration is the nature of the immobilized enzyme product which will be suitable for the collection of the organophosphates in the electrochemical cell as shown in Figure 1. After deciding that we were going to use horse serum cholinesterase as the enzyme sensor, the question that remained to be answered was the kind of support and the method of enzyme attachment to be used. In the report of bauman *et al.*[10] a procedure for the attachment of cholinesterase to sheets of open-pore polyurethane foam with starch gel was described. The resulting immobilized enzyme product was cut into cylindrical pads 3/8 in. diameter and 1/4 in. thick. Enzyme pads of this type have been used in the electrochemical cell; individual pads having an activity of 0.01 to 0.08 μ M/min/g have been used successfully in the detection system described in this paper. Some other enzyme pads with a similar high ratio of void spaces to solid spaces have been developed which are more retentive of their enzyme activity, and these will be described in a later report.

Design and Fabrication of the Continuous Aqueous Monitor, CAM-1

Before designing or constructing the water monitoring system based upon the use of immobilized cholinesterase as the sensor, it was necessary to consider the intended use of the detector, the manipulations and skills to be required of the operators, the period of unattended operation desired, the sensitivity, the selectivity, the permissible size, weight and cost, the need for maintenance, and other parameters affecting the design. From the beginning it was decided that 110V AC power would be available, and that the initial model would be operated indoors so that there would be no need to provide insulation and case heaters. It was hoped that unattended operation might be as long as a week, but 48 hrs was chosen as the immediate goal. It was hoped that the weight could be kept below 50 pounds and the volume below 2 cubic feet; it was our thinking that a smaller instrument would be much easier for the operator to use.

It was decided that if the instrument were to function unattended for long periods of time, every operation should be made as nearly automatic as possible. Of particular importance was a provision for an automatic enzyme pad changer and an automatic detection cycle which would signal an alarm when toxic hazards were present in the water sampled. We felt that the enzyme itself would give the unit selectivity since materials which inhibit this enzyme are likely to be toxic. Speed of response to inhibitors and sensitivity to low levels of inhibitors are dependent variables; it was obvious that longer sampling times would give the greatest sensitivity, but as shown after the unit was fabricated, a 2-minute water sampling period is adequate for the detection of subtoxic levels of organophosphates.

The Continuous Aqueous Monitor (CAM-1) which we have designed and fabricated for the rapid detection of organophosphates in water supplies is shown in Figure 2. Examination of the photograph and the call-outs will show that the automatic pad changer-electrochemical cell assembly is mounted at the bottom front of the cabinet with an access door. A closer view of this important part of the detection system is shown in Figure 3; it will be noted that one stepping motor is used to operate the chain drive for opening and closing the electrochemical cell, and another stepping motor for positioning the disc containing the enzyme pads. Eleven enzyme pads may be loaded into this disc at one time, and they are advanced automatically as necessary. Also located in the lowest compartment of CAM-1 (Figure 2) are the water and substrate pumps. The water pump has three movable impellers which are held against the inside of the pump housing by centrifugal force; this pump is self-priming and delivers about 1000 ml/min through the electrochemical cell. A peristaltic pump head turning at about 4 rpm is used to deliver 1.0 ml/min of substrate solution; this solution consists of 2.5 M × 10^{-4}M butyrylthiocholine iodide (BuSChI) in 0.08 M tris buffer, pH 7.4. Approximately 1 liter of this solution is needed for 48 hours of detector operation. The tris buffer ingredients and the BuSChI are estimated to cost about 40¢/liter; the enzyme pads can probably be made for less than 10¢ each.

Also located just to the right inside of the front door are the manual controls for the operation of the detection system. The top switch permits the electrochemical cell to be opened for replacement of the enzyme pads. Other manual switches permit the independent operation of the water pump, the substrate pump and applied current and are used for checking out the system during start-up of the detector operation.

On the second level of the detector are located: the recorder, the horn, the controls, the indicator lights, the warning lights, the DC power supplies, the constant current circuit and the air pump. On the third and uppermost level of the CAM-1 are located the relay board, the digital voltmeter which is used to indicate the cell voltage and also, as an

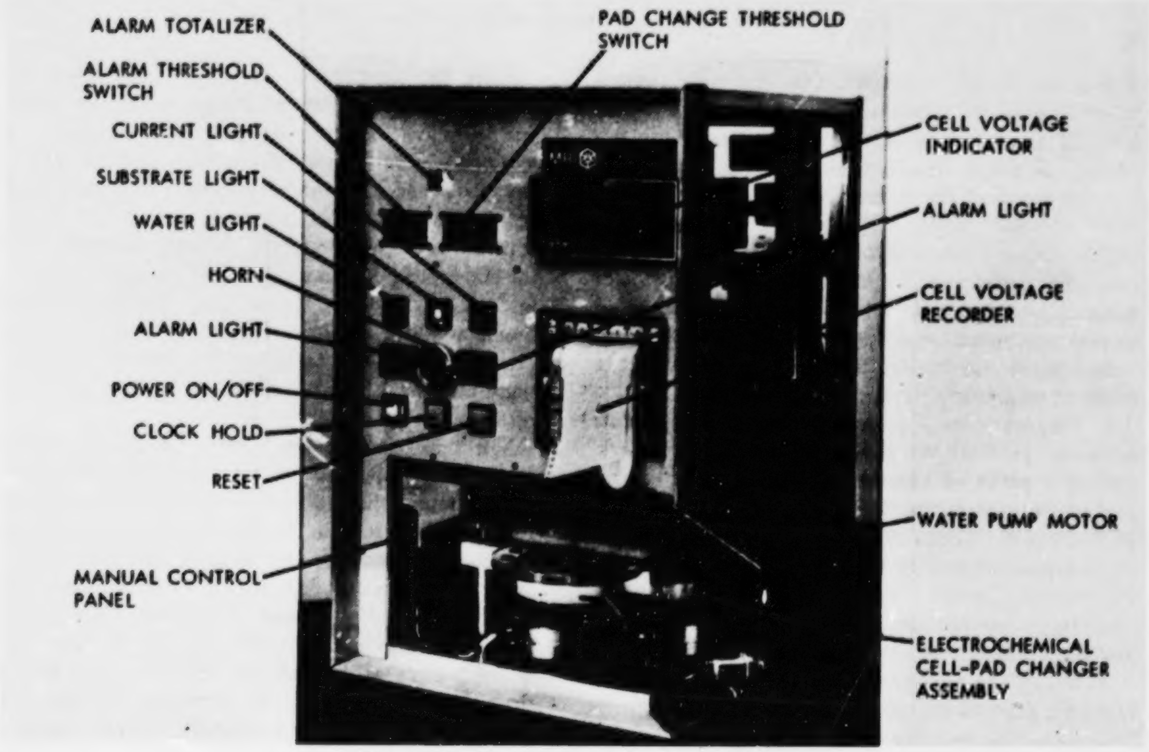


Figure 2: Continuous Aqueous Monitor (CAM-1)

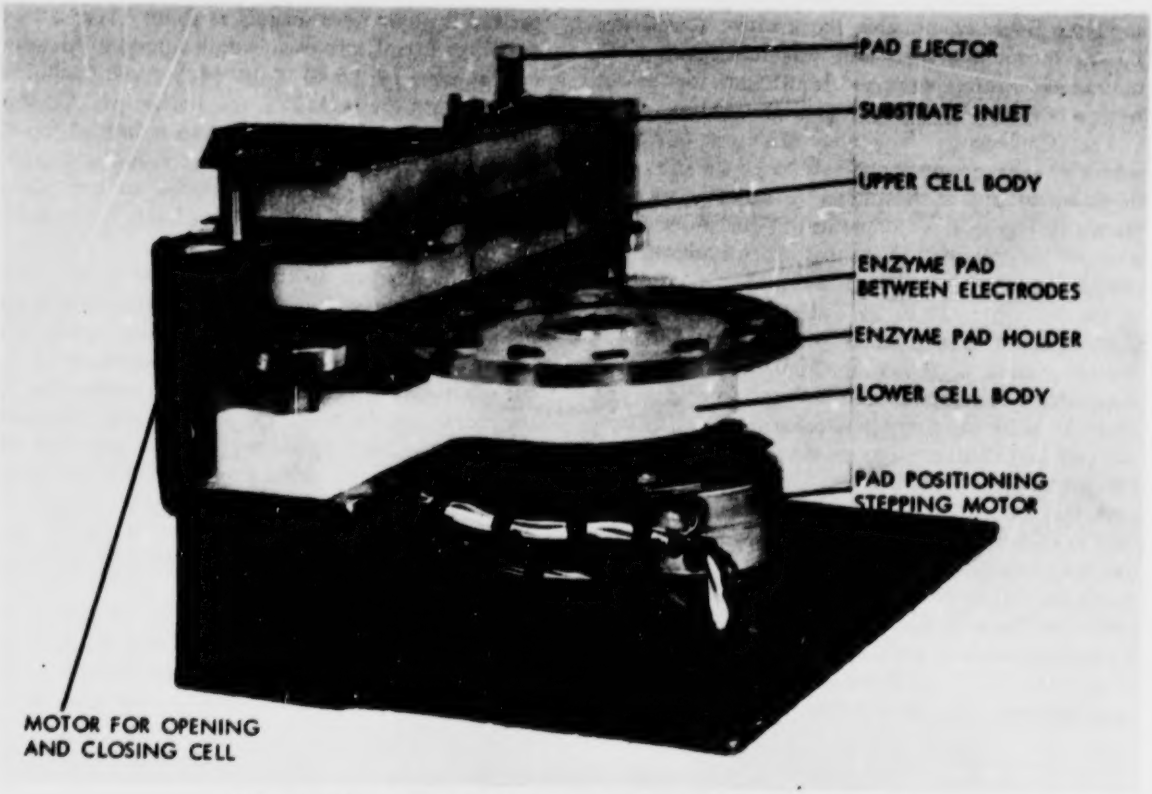

PAD EJECTOR
SUBSTRATE INLET
UPPER CELL BODY
ENZYME PAD BETWEEN ELECTRODES
ENZYME PAD HOLDER
LOWER CELL BODY
PAD POSITIONING STEPPING MOTOR
MOTOR FOR OPENING AND CLOSING CELL

Figure 3: Automatic Enzyme Pad Changer and Electrochemical Cell Assembly

analog to digital converter, the threshold switch used for automatic replacement of the enzyme pad when it is exhausted, the threshold switch for signaling an alarm and a totalizer (not shown) for keeping track of the number of alarms which have been signaled while the operator is away, the digital circuitry for controlling the operation of the detection cycle and the digital logic circuitry for deciding whether to sound an alarm, change pads or to continue operation on the usual cycle.

In order to use this detector, the operator would be required to perform the following operations:

1. Prepare a fresh solution of buffered substrate solution—perhaps by filling a bottle to a mark, adding a pellet of substrate and buffer ingredients and stirring for a minute. The substrate hose (back of instrument) would then be inserted into the substrate container and the substrate pump started using the manual control.
2. Insert enzyme pads into the enzyme pad holder and place them in the electrochemical cell.
3. Prime the substrate and water lines by operating the detector manually for five minutes.
4. Select the detector sensitivity desired.
5. Switch to automatic operation.

After the detector is started all operations are automatic. The different pumps, solenoid valves and applied current switches are activated in sequence by a digital clock; the enzyme pad is changed when it no longer possesses enough enzyme activity to provide an adequate safety factor. The constant current is applied twenty seconds after the substrate pump starts; the cell voltage is entered into the memory register at the appropriate moment and compared with the voltage from the previous cycle, and an alarm is sounded if the voltage change between cycles is larger than the operator-set threshold alarm value.

The operation of the CAM-1 produces cyclical changes of potentials of the electrodes in contact with the immobilized enzyme product as shown in Figure 4. At time 0 in the detection cycle the applied current is turned off, and water is pumped through the electrochemical cell with a resulting sharp fall in the electrode potentials. After two minutes have elapsed the water is turned off, the air and substrate pumps are turned on resulting in a further drop in cell voltage. After pumping air and substrate for 20 seconds the constant current system is connected, and there is a rapid rise in cell voltage

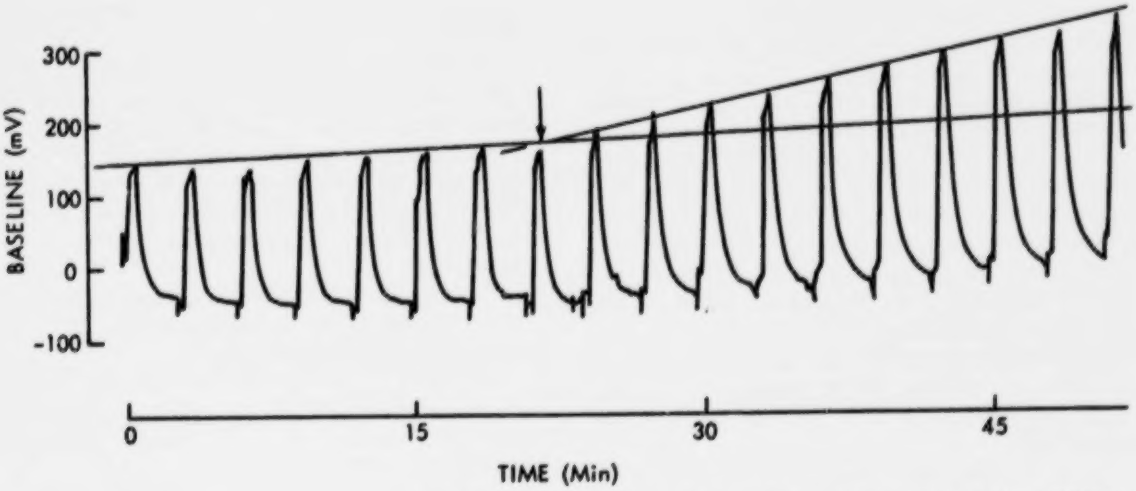


Figure 4: Response of the Electrochemical Cell Operating on the 3-Min Cycle (See Text) to Water Containing 0.2 ppm DDV(P

to a maximum which is related to the quantity of enzyme activity present. After the cell voltage has reached a value indicative of the amount of enzyme activity, the cell voltage is held on the digital voltmeter and also loaded into the memory and processing registers. At this time the current is turned off and the cycle begins again.

As shown in the tracing (Figure 4), there is a little voltage fluctuation between individual cycles (exaggerated for the purposes of illustrations) and also a gradual upward drift of the voltage maxima. In order to avoid false alarms it is necessary to set our alarm threshold (i.e., the difference in voltage between successive cycles), high enough so that the drift and the normal fluctuation will not activate the alarm. On the other hand, the alarm threshold should be set low enough so as to obtain the desired sensitivity to enzyme inhibitors. In the present example, a water supply containing 0.2 ppm of DDVP was pumped through the system starting at the end of the 7th complete cycle. During the next ten cycles there was an increase of 182 mV or an increase of 18.2 mV/cycle. This experiment shows that an alarm threshold of 12 mV/cycle would have given no alarm in the absence of the DDVP and an alarm for each of ten cycles in the presence of 0.2 ppm DDVP. Cell voltage increases of 20 to 60 mV/3-minute-cycle are not uncommon when higher concentrations of DDVP are present. As may be seen from this example, it is often possible to obtain several alarms from a single enzyme pad.

SUMMARY AND CONCLUSIONS

An automatic system for monitoring water supplies for the presence of organophosphates has been designed and fabricated for the first time, and it has been designated as the Continuous Aqueous Monitor (CAM-1). It has been fabricated so recently that little laboratory or field testing has been completed with it. In one response test with city tap water to which 0.2 ppm of DDVP (dimethyl-2, 2-dichlorovinyl phosphate) had been added, CAM-1 provided both audible and visual alarms repeatedly. The following rough calculation shows that this sensitivity is more than adequate for the protection of individuals using the water supplies: If we assume the LD_{50} of DDVP in man is 6 mg/kg (Heath[11] reports the LD_{50} for rats is 6 mg/kg and the Canada Department of Agriculture[12] reports the LD_{50} for rats is 56-170 mg/kg) and also that a man weighs 70 kg, then we see that a man would need to drink 4,200 liters of water containing 0.2 ppm of DDVP in order to receive the LD_{50} dose—an obvious impossibility. CAM-1 need not be operated at this high sensitivity; to lower the sensitivity all that is necessary is to increase the allowable voltage change between successive voltage measurements by adjusting the digital switch on the front of the instrument.

We do not know from experience how long individual enzyme pads can be made to perform in the presence of polluted water. In one test on raw Missouri River water at Kansas City, we passed 10 gallons of water through an enzyme pad and could not detect the loss in enzyme activity. In another test we pumped city tap water through a single enzyme pad for 68 hours; in this test more than half of the enzyme activity was lost, but there was enough residual activity so that it could have produced an alarm in our instrument. On the other hand, the life of the enzyme pad can be quite short in the presence of large quantities of enzyme inhibitors. Until we get experience operating the detector for extended periods of time in a variety of raw water supplies, we will not know how long the 11 enzyme pads loaded into a single unit may last.

Only limited interference studies with the CAM-1 unit have been conducted. However, since we have separated the inhibitor-collection cycle from the enzyme-monitoring cycle, we anticipate that some of the water impurities such as salt, reducing substances, etc., which might produce electrochemical changes in the electrodes, will be washed out of the cell before enzyme activity is measured. Studies of detector performance in the presence of various water pollutants other than the organic phosphates are needed.

Because of the need to monitor water continuously it was decided that two electrochemical cells operating out of phase would be required. Rather than placing both cells in the same cabinet we decided it would be better to use two CAM-1 instruments operating out of phase (i.e., one unit starting to sample water 90 seconds after the other). Provision has been made so that with a connecting cable the clock in either of two instruments can be used to control the detection cycles in both instruments. This arrangement has the advantage that it provides redundancy; in case an alarm is signalled in one instrument it will be possible to confirm this alarm signal within 90 sec.

We anticipate that it will be possible to make CAM-1 respond to a large number of hazardous materials by making changes in the enzyme and the substrate; these studies are now under consideration.

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AN AERIAL SURVEILLANCE SPILL PREVENTION SYSTEM

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ABSTRACT

A spill prevention system, using small scale color infrared photos and large scale color photos, has been developed for early warning of potential spills into waterways of oil and other hazardous substances. Detailed photo interpretation can locate careless practices or weakened structures associated with oil refineries and industrial activities and leading to corrective actions. Thermal infrared imagery has very limited application to spill prevention.

INTRODUCTION

Unplanned releases and accidental spills of oil and other hazardous materials into waterways cause many of the nation's serious water pollution problems. It can be shown by evaluating both the economic factors and environmental influences of spills that prevention is less costly than clean-up. If by comprehensive and intensive surveillance of industrial areas situated close to waterways potential sources of spills can be detected and corrected, many serious spills can be prevented.

For those spills that are associated with a stationary source, such as from facilities and structures, rather than a moving source such as ships, trains or other vehicles, periodic surveillance can in fact identify specific examples of careless practices which occasionally lead to spills. Herein lies the problem. In order for environmental control agencies to inspect all of the potential problem areas at prescribed intervals by conventional ground techniques, a sizable force of field personnel, vehicles and commensurate budget appropriations would be required.

It was hypothesized by the Environmental Protection Agency (EPA) that remote sensing systems using state-of-the-art technology could detect and identify potential sources of spills of oil and other hazardous substances, as well as delineate areas where no present threat of spills exists. By this approach considerably more efficient use of manpower and fiscal expenditures could be enjoyed. Furthermore, the time to complete a survey of industrialized areas would be far less using remote sensing methods than conventional ground methods.

For a remote sensing spill prevention system to be most effective it would be necessary first to determine the specifications for image acquisition, the flight parameters for aircraft operations and the image interpretation techniques that would optimize the location of potential spill sources. If all steps had been completed as planned, the output from such an approach would be a list of specific features and objects that, if left uncorrected, could possibly cause spills. The exact location of these features would be plotted on maps or photographs. Ground checking would be necessary only in those areas where definite indications of potential spills exist, thus optimizing the expenditure of manpower by eliminating from further concern many areas where no apparent spill threat exists.

The term remote sensing, as used in this paper, refers to the obtaining of information about an object or feature where the information gathering device is not in contact with the feature being observed. An aerial camera is a commonly used remote sensing device.

Two great advantages to using remote sensing devices to record information are that the limited spectral sensitivity of the human eye is expanded significantly and the absence of magnifying power of the human eye is overcome. Furthermore, the human observer, unaided by remote sensing devices, must commit to memory or to some form of manual recording—writing or voice recording—the information he sees as he flies over a target area. On the other hand, by the use of remote sensing, a hard copy such as a photograph may be obtained for future detailed study in the observer's office, often in the presence of experts operating with visual aids and reference materials.

A demonstration project was undertaken under the sponsorship of the EPA to devise the best means to prevent spills by an early warning system using remote sensing.

Demonstration Project

For the demonstration project an industrialized region, the San Francisco Bay area, which contained typical spill threats from oil refineries, chemical plants, heavy and light industrial facilities, and waste treatment operations was selected. That the area selected was suitable for this demonstration became apparent when evidence of several recent spills and currently active discharges were encountered during definition of specific test areas in the early phases of this project.

Because the objectives required the use of state-of-the-art remote sensing equipment, a camera system was selected which used readily available films and filters and which, for the purposes of this study, could obtain several film-filter combinations simultaneously. A four camera array of 70mm Hasselblad 500 EL cameras was used to obtain photos on four film-filter combinations (color, color infrared with Wratten 12 filter, pan plus-blue with 47B filter and black-and-white infrared with 89B filter) to select the one or ones most useful for detecting potential spill threats. For purposes of speed and economy it was suggested that initially a regional survey would be conducted to delineate areas of interest for further detailed study, while eliminating from further study areas which contained no features of interest.

Photographs were taken at several scales (1/2,500, 1/5,000, 1/10,000, 1/20,000, 1/40,000 and 1/80,000) for a test to determine the most useful scales for the regional (small scale) study and local (large scale) study. Information derived from the investigation of optimum scale was used to specify flights over several test areas in the San Francisco Bay area. These areas were selected to cover a variety of potential spill problems.

A photo mission was first scheduled over each test area taking small scale (1/40,000) color infrared photography. These photos were interpreted, and recognizable ground features, facilities and structures were classified according to a scheme that related to industrial activities and associated waste materials (see Appendix). Areas where industries typically associated with spills of oil or other hazardous materials are located were delineated for further photo coverage at large scale.

Flight lines were laid out and large scale (1/10,000) coverage was obtained using aerial color film.

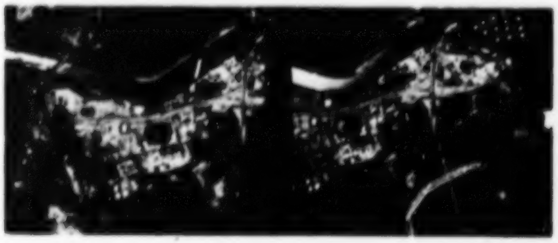

Figure 1a: Panchromatic Plus-Blue (47B filter), 1/40,000. Note proximity to waterway. This scale is useful for regional surveys.

Figure 1b: Oil storage tanks. Panchromatic Plus-Blue (47B filter), 1/40,000. Note catch basin for overflow of oil.

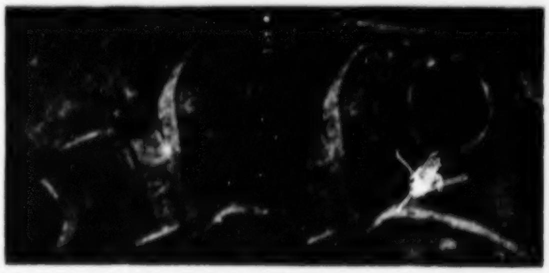

Figure 1c: Catch basin seen in photo above. Infrared (89B filter), 1/2,500. Pond is covered with diesel fuel from tank at right

Figure 1: Oil Refinery at Avon, California (Stereo View)

Detailed interpretation was performed on the large scale photos in which features such as levees, fences, pipelines, pumps, oil loading areas, waste piles, ore piles, holding ponds and outfalls could be seen and evaluated (Figures 1 and 2).

When interpretation of any of these features indicated that they were in a state that could contribute to a spill they were marked for ground checking and low altitude oblique photo coverage. In some cases the threat was so obvious that ground checking was not warranted.

In addition, thermal infrared flights were made using an RS-14 scanner operating in the 8-14 micrometer range. Data was acquired in the afternoon, late evening and after midnight.

The use of a thermal infrared scanner was expected to reveal areas where heated discharges or leaks from holding ponds, pipelines or tanks occurred that might not be visible on conventional photography.

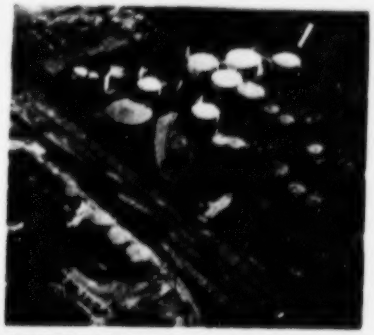

Figure 2a: Storage tank at upper right is unrevetted and could cause spill into waterway. This area is seen on upper photos of Figure 1.

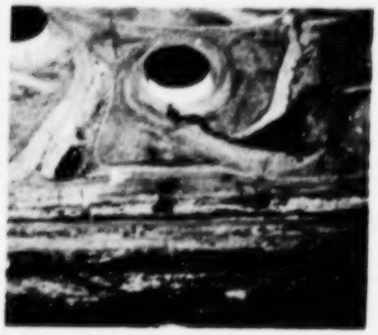

Figure 2b: Oil catch basin seen in lower photos of Figure 1.

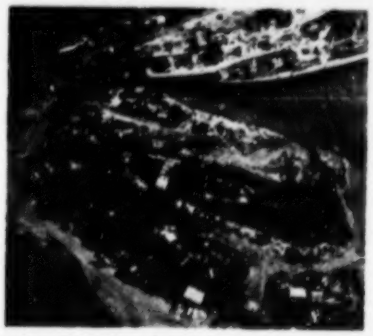

Figure 2c: Scrap steel salvage operation waste deposits on shoreline causing potential contamination of waterway. Richmond, California

Figure 2: Oblique Views of Potential Spill Problems

SUMMARY AND CONCLUSIONS

This project demonstrated conclusively that, as first step toward its objective of spill prevention, remote sensing could be used to delineate areas where oil refineries and industries are located, using small scale (1/40,000 to 1/60,000) color infrared/Wratten 12 photography. It further demonstrated that large scale (1/5,000 to 1/10,000) color aerial photography, taken of probable high hazard areas as detected on small scale photography, could provide detailed information on specific spill threats as well as active spill sources. Many spill threats were detected and correctly identified (as verified by subsequent ground checking) using the techniques developed in this study. Documentary low altitude oblique color photographs were taken in most instances to verify findings made on high altitude vertical photography.

Careful and comprehensive photo interpretation was shown to be an important part of this spill prevention system. A land use and industrial facility classification was made based on a scheme compiled for this study. The scheme and an accompanying photo interpretation key permitted an interpreter to separate various refinery and industrial facilities, known to be spill sources of oil and other hazardous substances, from those features not usually associated with spills.

Furthermore, specific locations of spill threats could be identified and their degree of hazard assessed including, for example, unrevetted storage tanks, unprotected pipelines exposed to vehicle traffic along highways, waste piles carelessly handled along shorelines, evidence of past oil spills on land adjacent to waterways, chemical plants and canneries that discharged into sloughs leading to major waterways, and shorelines industries dumping waste materials into waterways. Thermal pollution was detected using an airborne thermal scanner.

Capacities of storage tanks and surrounding revetments were measured by photogrammetry.

It was shown that careful flight planning is an essential part of obtaining satisfactory aerial surveillance coverage for spill prevention. Flight line placement, altitudes, times of day or night and equipment parameters are essential items to be considered in flight operations. A trained photo interpreter should be involved in all flight planning and in specifying photographic and thermal sensing flights.

Spill prevention requires a periodic assessment of practices, facilities and environmental characteristics associated with oil refining and industrial activities to detect potential unplanned or illegal release of materials into waterways. This assessment must be comprehensive, complete and detailed. It cannot be done by a sampling procedure but requires a look at all possible sources of spills—a 100% survey.

It does not appear that ground observation of industrialized areas will accomplish the needed assessment because of time constraints, economic factors, inaccessibility, and the inability of a ground-based survey to detect water quality conditions that reveal potential spill sources.

It has been demonstrated that remote sensing will provide a means to detect and identify a significant number of potential spill sources thus permitting ground personnel to take corrective action before a serious spill occurs.

APPENDIX

Classification Scheme

Static Facilities

Tank farms
Raw material, byproduct or waste piles
Waste lagoons and cooling ponds
Terminals
Pumping stations
Refining & processing installations
Power plants
Pipelines
Slaughterhouses
Livestock pens
Junk yards
Garbage dumps

Transient Facilities

Railroad cars
Trucks
Grading equipment
Ships

Activities

Mining
Transport
Storage
Manufacturing
Refining and processing
Waste treatment and disposal
Land development
Forestry
Agriculture
Recycling

*Materials**

Solid
Liquid
Gas
Thermal

Protective Features

Dikes, levees, dams
Barricades and railings
Revetments
Moats and trenches
Automatic control devices
By-pass storage
Cooling ponds and waste lagoons
Derailing prevention devices
Channel markers
Floating barriers

Evidence of Previous Problems

Immediate Past

Vegetative alterations
Stains
Turbidity
Slicks
Fish kills
Thermal anomalies

Remote Past

Drainage patterns
Vegetative alterations
Stains
Residues and deposits
Thermal anomalies

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*Photo interpretation will yield only these categories plus identification of material as raw input, output or by-product. Ground truth will provide specific identities such as chemical composition, radioactivity, etc.

STRATEGY FOR TREATMENT OF WATERS CONTAMINATED BY HAZARDOUS MATERIALS

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INTRODUCTION

Response procedures designed to mitigate the effects of hazardous material spills involve a complex blend of expertise and equipment. Personnel must conduct activities dealing with detection, identification and monitoring, water treatment or containment, environmental restoration, damage assessment, and regulatory review. Of these, identification, monitoring, and damage assessment are the most intimately tied to the treatment phase of the response program.

Upon detection of a spill, prospects for an effective response rest in part on the ability to identify the materials released. Correct identification of the contaminants involved enables both an evaluation of the nature and extent of the hazard, and an assessment of what types of amelioration techniques may prove effective.

Although very sophisticated analytical techniques have been developed to perform this function, they often require large, sensitive equipment, trained personnel, and complicated procedures. Typically, these may be unavailable at or near a spill site. Consequently, time is lost in the identification phase and the prospects for minimizing damage by quick response are also lost. On the other hand, proceeding prematurely when little is known of the nature of the spilled material can result in wasted effort and injury to personnel.

Monitoring the spill to chart its diffusion and translocation through the aquatic environment may often be more easily accomplished than identification. Once the exact nature of the contaminant is ascertained, gross detection techniques can be employed to monitor the resulting plume. These may include TOC, pH, conductivity, or specific electrode measurement techniques. Although a degree of sensitivity is sacrificed, simplified detectors can provide rapid *in situ* methods to locate the areas to be treated and assess the effectiveness of the countermeasure employed.

Damage assessment analysis is required for considerations other than liability allocation. A properly designed assessment program can be used to evaluate the benefits of the countermeasure employed as well as any hazards inherent in the countermeasure itself. As information in this area is compiled, guidelines can be developed for better use of treatment techniques in the future.

Response Techniques

Potential treatments which conceivably can be applied to ameliorate the effects of hazardous polluting substances in the aquatic environment are almost equal in number to the substances themselves. Obviously, it would be impractical to attempt to develop a specific countermeasure for each individual hazardous polluting substance. Moreover, since the resources which can be invested in developing countermeasures against hazardous polluting substances in the aquatic environment are limited, efforts must be directed toward those areas which promise to produce the maximum return on this investment.

The following criteria is suggested for evaluation of potential countermeasures:

- Countermeasures should be highly effective.
- Countermeasures should be applicable to a large number of substances.
- Countermeasures should be amenable to rapid, easy deployment. Highly specialized equipment and/or chemicals which require wide deployment and stockpiling prior to a pollution

incident or which cannot be rapidly conveyed to the scene of an incident are undesirable.

- Countermeasures should be free from potentially harmful secondary effects in the aquatic environment, including noxious sludges.
- Countermeasures developed to combat spills of hazardous polluting substances should take advantage of existing technology, particularly that technology developed to combat oil spills, to the maximum possible extent.

Treatments which could be considered include chemical degradation, precipitation, neutralization, physical adsorption, complex formation, ion exchange, solvent extraction, foam separation, and biological degradation. Several of these can be eliminated because of the threat of secondary effects from the required additives and reaction products.

- *Chemical degradation* (transformation, oxidation-reduction, etc.) is generally unacceptable, since in most cases the agents that must be added to effect reaction pose an equal or greater potential hazard to the aquatic environment than the original pollutant. The situation is further complicated by the nature of the spill environment which does not allow close control of operating conditions. Concentration changes resulting from natural dilution processes could cause excess chemical addition, and so increase the damage to the aquatic environment.
- *Complex formation and neutralization* suffer from similar difficulties related to not controlling the reaction environment and the inherent threat to water quality of the necessary additives.
- *Precipitation techniques* at first appear to be an attractive solution; however, the ultimate reaction poses a new type of threat. Lacking an effective means for removing the precipitate, the watercourse is subjected to a concentrated buildup of fine particulate matter which could damage feeding and spawning grounds with subsequent deleterious effects on aquatic life. The full impact of this type of damage has never been satisfactorily explained, but presumably it could rival the damages of the original pollutant to water quality. Further, the introduction of colloidal precipitates would still threaten gilled species and would decidedly reduce recreational and aesthetic benefits. While development of a subsurface collection device along the lines of a swimming pool vacuum would alleviate these effects, the enormous operational problems associated with such an approach are obvious.
- *Solvent extraction and foam separation* processes have several intriguing characteristics. Through proper choice of solvent, the product stream can be made to rise to the surface where ready collection with existing hardware should be possible. In addition, solvent extraction and foam separation processes are fairly broad-based, with a single component displaying applicability to many pollutant releases. Unfortunately, both processes require some control over the area to be treated, and treatment of any large body of water would necessitate use of several types of feed mechanisms. This implies high capital costs and storage facilities to stockpile such equipment regionally. Further, in the case of solvent extraction, a large quantity of solvent would be required to achieve only reasonable removal efficiency.
- *Vacuum or dredging* systems for sunken materials are speculative. The swimming pool vacuum system may be a workable concept, but there is also a good chance that to effectively remove the contaminant, a large quantity of benthos would also have to be removed and handled. While heavy flocs and precipitates may prove innocuous enough to be left on the bottom, heavy liquids are a separate consideration. They pose a threat to water intakes which may be located near the bottom of a water source. For example, in the event of a spill, a substance such as ethylene dichloride would seek the bottom without dissolving.
- *Skimming and booming* are available techniques for oil spills. They could be applied to light insoluble materials as well as slightly soluble organics. Rapid response aimed at booming and skimming any undissolved portion of the contaminant could greatly reduce the severity of a spill.
- *Flow augmentation* can be applied only in certain circumstances. Mechanical mixers such as outboard motors can be used to aid diffusion. Flow augmentation may be utilized where stored water is available upstream. In any event, such a practice is reliant in part on good predictive models of the aquatic environment to determine the extent of contamination and expected duration of toxic concentrations. This information is available for a number of streams, as is time-of-travel data. Such data are not gathered in a single source nor properly referenced to allow for quick retrieval and application in a practical emergency, however.
- *Burn off* techniques are probably applicable only in very limited cases where the material remains confined in a small isolated area so as

to minimize threats to safety and air quality. Many hazardous materials emit highly toxic vapors when heated to decomposition. Consequently, burning may intensify hazardous conditions and force evacuation of areas surrounding a spill site. The presence of heavy vapors which can travel along the ground and cause flash-backs further endangers safety when burn techniques are applied.

- *Oxygen addition* may be an attractive alternative available for substances posing a BOD problem. The oxygen is added to the water to maintain dissolved oxygen levels while a spilled material is being dispersed and degraded aerobically. There has been recent interest in injecting air or pure oxygen into water courses to achieve this end in areas of chronic low dissolved oxygen. The required apparatus is simple enough that mobilization for transport to a spill site should be possible. The problems would be those involved with supplying enough gas to accomplish the task and designing equipment that could efficiently transfer the gas into a variety of potential stream or reservoir configurations.
- *Biological degradation*, while attractive in some respects, suffers from several difficulties. In order for degradation to proceed at a rapid rate, it would be necessary to have on hand large quantities of acclimated cultures. The problems associated with stockpiling many such cultures, each of which is specific to a particular substance, are obvious. Also, many hazardous materials are inherently resistant to biological degradation.
- *Physical sorption and ion exchange* apear to offer the greatest promise for treatment of acute spills in the aquatic environment. Sorption and ion exchange processes rapidly remove substances from solution and hold them in a relatively innocuous form for long periods of time. The use of exchange resins for acid, base, metal, or toxic salt spills and the use of activated carbon or sorption resins for organic matter could apply to a large number of hazardous polluting substances with varying degrees of efficiency. The two major problems associated with the application of mass transfer media to counteract hazardous polluting substances in a free water environment are:
  1) the mechanics of introducing the active media into the water, and
  2) the subsequent removal of the media from the water.

Traditionally, such processes have been restricted to operation within columns. This method of application is limited by some very real concerns: the cost of stockpiling mobile columns for spill treatment, the problem of rapid deployment of the large equipment involved, and the practicality of pumping free waters into a contained environment for treatment. Some studies have been conducted with powdered activated carbon in which the sorptive media was dispersed in the water and allowed to settle. The basic premise of this work was that the carbon is innocuous to aquatic life and can be allowed to settle. Although this may be true in selected impoundments, in flowing streams the aesthetic damage would be extensive and gilled species would be subjected to the problems inherent in an environment highly saturated with particulate and colloidal matter.

Spill Dynamics

Whatever mode of treatment is selected, consideration of spill dynamics is essential to maximize the benefits from a response. The dynamics of a release are dependent both on the mode of entry and the physical characteristics of the material.

- Gases may rise rapidly and disperse or hover over the water providing a continuous source for equilibrium levels of the material in surface waters.
- Liquids may float in slicks, slowly dissolving into the water; rapidly assimilate into the aquatic environment and go through normal dispersion patterns; or sink to the bottom and slowly dissolve into the water.
- Solids can follow the same pattern as liquids or can form fine suspensions in the water evidencing themselves as a turbid cloud.

The individual route or combination of routes experienced in a spill situation will affect the kinetics of any countermeasure employed. It is desirable, however, that the success of a response technique would not depend upon any single mechanism.

The nature of the body of water affected by a spill also has a great effect on the type of response that can be made. Small impoundments, where damage is believed to be complete (e.g. total fish kill), can be subjected to efficient but harsh chemical countermeasures since extensive restocking will be required anyway. Water from small impoundments can also be pumped through exterior facilities for treatment. Small streams and bodies of moving water can be dammed and routed through treatment facilities with the use of portable coffers and culverts. Large bodies of water pose the most challenging problems, since the entire volume affected by a spill can not be practically controlled or managed. In these cases, response measures must be carefully scrutinized to avoid intensifying or augmenting damage to aquatic life through the use of improperly chosen techniques.

Ultimately, the most vital parameter in the determination of the success of a response is the time lag between the spill and the initiation of the treatment phase. Concentration-time lethality curves drawn for individual contaminants to aquatic life suggest that even high doses of hazardous materials can often be tolerated for short periods of time. This would be the case where transfer of contaminant across the gills of fish is the limiting step such that lethal amounts could not physically be absorbed in the given time period. Conversely, low concentrations can be lethal over prolonged exposure periods due to bioaccumulation or cumulative effects.

Most candidate response systems exhibit much higher efficiencies at higher concentrations. Hence, the benefits derived from a set level of treatment expense (e.g. a given quantity of chemical) are greater as the delay is shortened so that natural diffusion has not reduced concentrations to levels where treatment efficiency is poor. Rapid response also reduces the volume of water requiring treatment and offers greater assurance that few water supply systems will be jeopardized by intrusion of the spilled material.

SUMMARY

The field of *in situ* treatment of waters contaminated by hazardous materials is in the formative stages. Exploratory work has been completed and has laid out an extensive blueprint of field evaluations, research, and development which must be performed to complete the formulation of a strategy for response. Initial findings suggest that work is especially required in the areas of pollutant identification, spill monitoring, damage assessment and specific treatment concept development.

Methods are available for removing almost all water contaminants under controlled conditions. However, many of these techniques are not satisfactory for application in the aquatic environment. In most cases, there are uncertainties as to the secondary effects of those measures considered potentially effective (e.g., the environmental effects of sludges resulting from countermeasures may be more harmful than the original hazard). The answer to the problem of positive response to a spill must come from one of two directions: either new methods of treatment must be developed, or new methods for controlling the aquatic environment must be established.

Time is perhaps the most critical factor in spill response. Damage and time are linked through an exponential relation which puts a premium on response practices that can be enacted immediately. This requires a highly efficient reporting structure as well as countermeasures developed with quick deployment in mind. Programs must therefore be undertaken with speed of response as a major objective.

A SHORT CONTACT TIME PHYSICAL-CHEMICAL TREATMENT SYSTEM FOR HAZARDOUS MATERIAL CONTAMINATED WATERS

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and
T. G. PANTAZELOS
STANLEY R. RICH
R P Industries, Inc.

INTRODUCTION

This program is a feasibility study on the effectiveness of new devices to decontaminate spilled hazardous materials by short contact time treatment in a continuous flow configuration. The work was conducted by the coordinated efforts of scientists, engineers, biologists and chemists from Industrial BIO-TEST Laboratories, Inc., Northbrook, Illinois, and R P Industries, Inc., Marlboro, Massachusetts, supported by Contract No. 68-01-0123 from the Environmental Protection Agency.

The Battelle Report* on "Control of Spillage of Hazardous Pollution Substances" clearly documents the fact that techniques for treating and controlling the aquatic environment are inadequate or nonexistent. Methods are available as a second line of defense for removing almost all water contaminants under controlled conditions and with fixed water treatment plant installations. However, most of these techniques are not satisfactory for application in the aquatic environment. Work must be initiated in the area of control to develop new methods for containing spills before they reach surface waters, to contain contaminated waters after a spill, to decontaminate polluted water areas and to return the water in a restored condition of quality.

It is possible to partially contain spills by rapid dispatch of materials and equipment to erect temporary mechanical barriers. For example, sand, gravel, and cement trucks in a disaster spill area can be dispatched on relatively short notice and with the help of earth moving equipment could erect temporary dams, culverts and containment areas. Fire fighting equipment in the area could be dispatched for necessary pumping required to dilute or divert the partially contained spill if desired.

These measures are only common sense emergency procedures which may help in preventing sizable quantities of hazardous materials from reaching vulnerable waterways. These methods in themselves appear to be totally inadequate to effect a decontamination of the hazardous materials, a step which we feel is essential to the effective neutralization of a toxic material spilled in the environment.

While we recognize that emergency physical methods of containment are necessary and desirable, our effort is directed to the decontaimination of the contained spill and the contaminated waterway itself through a process of physical and chemical reactions carried out by a continuous flow thin-film gas-liquid-particulate contact device. With this configuration, it is possible to meter into the continuous flowing stream of contaminated water stoi-

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**Control of Spillage of Hazardous Polluting Substances*, G. W. Dawson, A. J. Shuckrow, and W. H. Swift, Battelle Memorial Institute, Program No. 1508, Contract No. 14-12-866, Nov. 1, 1970.

chiometric quantities of decontaminating agents in the physical form of gases, liquids, slurries and powders. These decontaminating agents interface with the contaminated water in thin film configuration and effect decontamination during the approximately one-second residence time in the reaction column.

The decontamination is effectively achieved by one or more processes involving oxidation, neutralization, precipitation or adsorption on powdered carbon. Design and operating details will also be given for gas stripping and solids separation methods. These techniques are used in continuous flow tandem sequence with the reactor to remove hazardous gases, precipitates, flocculates of carbon suspensions or other products of the decontamination process from the effluent of the reactor.

Description of Equipment

The continuous gas/liquid contactor, the Dynactor*, is a proprietary development of R P Industries, Inc. Figure 1 is a cross section of a single stage Dynactor diffusion contactor. Liquid entering the system under a pressure to 40 to 100 pounds per square inch (typical) is atomized into thin films and droplets of average thickness or diameter less than 1/64 inch. This liquid discharge diffuses or expands into the reaction chamber causing air or gas to be aspirated by being trapped within the moving shower of films and particles. The resulting mixed fluid then continues to travel down the reaction column with intimate contact maintained between gas and liquid. This causes physical and chemical equilibria to occur by the time the mixed fluid exits from the reaction column into the separation reservoir. The Dynactor can be viewed as a macroscopic diffusion pump which makes use of diffusion principles in order to aspirate large volumes of air per volume of motive liquid. By utilizing diffusion rather than Bernoulli principles, the Dynactor aspirates up to 4,800 standard volumes of gas per volume of motive liquid. In comparison, venturi eductors will aspirate not more than 100 volumes of gas per volume of motive liquid.

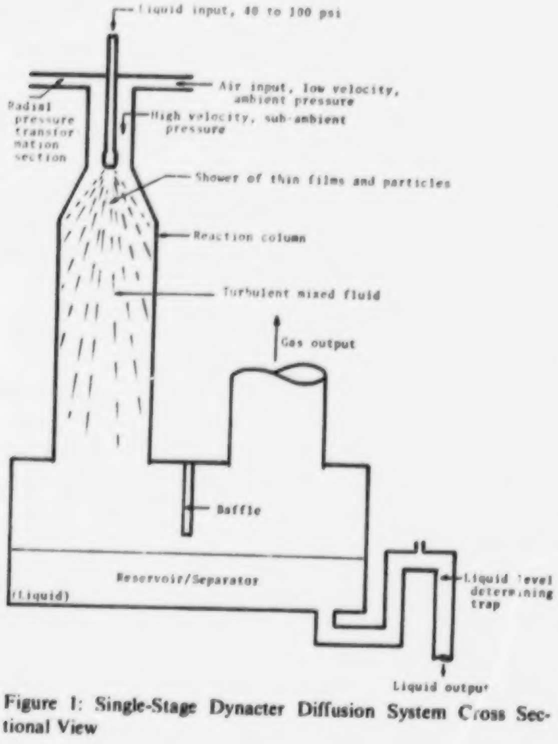
Liquid input, 40 to 100 psi
Air input, low velocity, ambient pressure
Radial pressure transformation section
High velocity, sub-ambient pressure
Shower of thin films and particles
Reaction column
Turbulent mixed fluid
Gas output
Baffle
Reservoir/Separator
(Liquid)
Liquid level determining trap
Liquid output

Figure 1: Single-Stage Dynacter Diffusion System Cross Sectional View

Because there are no venturi or other constrictions in the Dynactor, energy requirements are considerably lower than for conventional jet or venturi eductor systems. If gas carries small solid particles along with it, such as activated carbon or powdered neutralizing and precipitating agents, such particles are wetted and captured by the liquid throughout the entire length of the reaction chamber. By contrast, venturi wet scrubbers make effective contact between gas and liquid only in the constricted throat region. Contact time, therefore, in the Dynactor is about 20 times longer than in venturi devices.

Just as in oil and mercury diffusion vacuum pumps, it is also possible to construct Dynactors having multistage gas inputs. Figure 2 is a photograph of the two-stage Dynactor diffuser system employed in these studies. The internal configuration is constructed to maximize gas/liquid turbulence and contact throughout the length of the six-foot long, 12-inch diameter reaction column. The radial pressure transformation section shown in Figure 1 is used to transform ambient or atmospheric air pressure to the partial vacuum that obtains within the Dynactor. Entering air is accelerated from low velocity and atmospheric pressure to high velocity and sub-ambient pressure as it enters the reaction column.

The two-stage Dynactor employed in the present study uses an input of 4.2 gallons per minute of water at 100 pounds per square inch pressure. (All contaminants studied were in such concentrations that the physical properties of water itself prevailed in determining the operating parameters of the system.) At 4.2 gallons per minute, approximately 2,000 standard cubic feet per minute of atmospheric air is aspirated into the Dynactor and reacts with the liquid. Power requirements are 1/3 horsepower under these conditions.

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*Patent pending

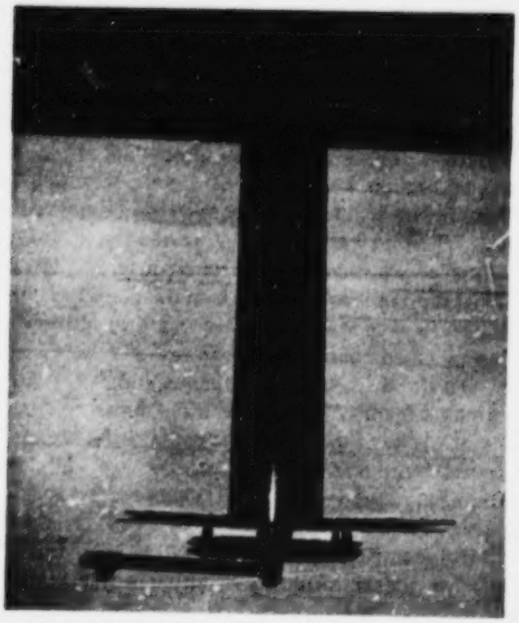

Figure 2: A Short Contact Time Physical-Chemical Treatment System for Hazardous Material Contaminated Waters

The Dynactor, much like oil or mercury diffusion vacuum pumps, has no moving parts. Since there are no constrictions, there are no zones or portions of the Dynactor on which solids or liquids tend to accumulate, thus requiring little maintenance. These units have been constructed in a wide variety of materials, including polypropylene, polyvinylchloride, stainless steel, and mild steel. Nozzle design is such that these elements tend to be self-cleaning, further reducing maintenance requirements.

The Dynactor's high speed chemical and physical reaction characteristics are due to its treatment of the flowing liquids essentially in thin film form. Its substantially instantaneous gas transfer (oxygen, chlorine, ozone), mass transfer (reaction with activated carbon, other reagents), and heat transfer (both evaporative and conductive) are seen from the following analysis:

Thermal Conductivity (Fourier's Law)

$$Q = \frac{K\,A\,(T_2 - T_1)}{h}$$

Q = heat flow/unit time
K = thermal conductivity
T_1 = temperature at boundary 1
T_2 = temperature at boundary 2
h = layer thickness
A = Area

Gas Diffusion (Mass Transfer)

$$\frac{m}{t} = \frac{B\,(d_2 - d_1)}{h}$$

= mass flow/unit time
B = coefficient of diffusion
d_2 = gas concentration at boundary 2
d_1 = gas concentration at boundary 1
h = layer thickness

As a consequence of their similar form, the solutions for both equations are also similar. There is obtained, therefore, from the solution of the heat-flow equation, the solution of the mass transfer equation when the dissolved gas concentration is substituted for the temperature, T, and the diffusion coefficient, B, for thermal conductivity, K.

In the applicable transient heat or mass flow problem in which a layer of thickness, h, having an initial (a) temperature, or (b) gas concentration, is subjected at one boundary to a higher or lower (c) new temperature or (d) new gas concentration, the Fourier Integral analysis and solution takes the form:

$$f(h,T) \text{ or } f(h,d) = \frac{1}{\text{constant}_1}\, e^{\frac{-h^2}{\text{constant}_2}}$$

It is seen that the solution involves an exponential term that includes the square of the thickness of the liquid layer as an exponent of e. Working through the mathematical details, it can be shown that a liquid layer of less than .01 inches thick reaches physical and chemical equilibrium with a contacting gas in less than 0.1 seconds.

Since decontamination reactions may result in precipitates, toxic gases and chemicals adsorbed on carbon in the effluent from the Dynactor, continuous flow separation methods and devices have been developed and evaluated. One of these devices is a static sealed centrifuge called a Statifuge, shown diagrammatically in Figure 3. Liquid is forced into a special vortex pattern characterized by extremely high centrifugal acceleration. The results are efficient solids separation on a continuous flow basis, and continuous vacuum removal of volatile gases, vapors and entrained gas.

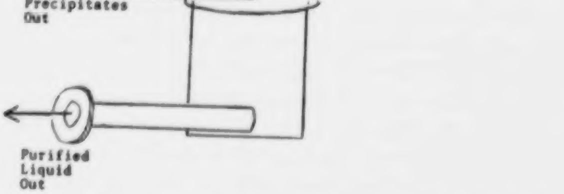

Figure 3: Statifuge—Static Centrifuge for Separation of Gases and Solids from Mixed Fluids

The solids separation is due to the high centrifugal acceleration, coupled with an efficient separation method. The vacuum removal of volatiles is made possible by a dynamic vacuum which is created within the fluid flow, causing volatile gases and vapor to be centrifuged continuously into this vacuum. Such gases and vapors are then removed by an external pump, leaving the main liquid stream free of the offending volatile contaminant.

Finely divided precipitates and suspensions of powdered activated carbon are flocculated and separated by a special process in a continuous flow configuration. Details of carbon floc separation methods will be presented at the National Conference on Control of Hazardous Material Spills in Houston on March 22, 1972.

Decontamination Experiments

Aeration

Since the Dynactor is a thin film aeration device capable of aspirating 4,800 volumes of air per volume of motive liquid, a typical flow-through experiment results in an effluent completely saturated with dissolved oxygen. Repeated experiments for oxygenation capability raised the dissolved oxygen concentration of water from one ppm to 10 ppm in a single pass through the Dynactor. Supersaturation of the effluent with dissolved oxygen was always achieved. Field samples of Des Plaines, Illinois, River water containing 5 mg/liter dissolved oxygen was aerated to 9 mg/liter (20°C) by passage through the Dynactor.

Simple, effective, continuous flow, high speed aeration of a waterway is in itself a significant contribution to water quality by increasing the dissolved oxygen content of streams, lakes, or lagoons. Many substances are toxic because they can threaten water quality by reducing the dissolved oxygen content. This can adversely affect aquatic life. There is general agreement that it is desirable to maintain high dissolved oxygen levels in water while the spilled material is being dispersed, decontaminated, and degraded aerobically.

Ozonation and Chlorination

The Dynactor used for gas experiments contains a plenum surrounding the top air intake section. The plenum has a 16-inch gas intake port which can be baffled to meter measured quantities of gases from compressed cylinders. The unit can also be used in a completely closed circulation system by connecting the gas outlet from the reservoir to the plenum intake port. Thus, ozone, for example, can be recirculated for optimum uptake and utilization by the thin film of water in the reaction column of the Dynactor.

Ozone was delivered to the sealed plenum of the Dynactor from a Welsbach Ozonator through a Tygon tube at rates of approximately seven liters per minute containing approximately 15 mg 0_3 per liter. Maximum absorption of ozone was demonstrated in the effluent. The conversion of potassium iodide to iodine was studied by processing 25 gallons of KI solutions through the Dynactor while bleeding measured quantities of ozone into the closed plenum. The iodine was quantitated by sodium thiosulfate titration. Complete conversion of KI to I_3 was achieved in a single pass through the Dynactor with significantly less than stoichiometric quantities of ozone. Further experiments using ozone to decontaminate phenol, cyanides, alcohols and other susceptible hazardous spill chemicals are in progress.

Chlorine and oxygen can also be metered into the Dynactor for thin film gas liquid contact where needed for oxidative decontamination of hazardous materials. These experiments are also in progress and will be reported.

Neutralization

Since the Dynactor is equipped with both a liquid metering system and a powder feed system, saturated sodium bicarbonate solutions and powdered sodium bicarbonate were individually studied as neutralizing agents for acetic and hydrochloric acids. Each form of bicarbonate effectively neutralized the acid representing the spilled hazardous material. For example, stoichiometric quantities of powdered sodium bicarbonate were aerosolized into the plenum of the Dynactor and instantly neutralized 0.01N acetic acid at a flow rate of 5 gpm at a head pressure of 100 psi. pH, titratable acidity and odor measurements were recorded on the effluent from the Dynactor to substantiate complete neutralization. Repeated experiments have been made with higher concentrations of acetic and hydrochloric acids with effective neutralization.

The successful use of powdered sodium bicarbonate, sodium carbonate and calcium hydroxide as dry neutralizing and precipitating agents in the continuous flow Dynactor configuration has proven the feasibility of this system for processing and decontaminating many spilled hazardous materials such as acids, alkalies and heavy metals.

Precipitation

Stoichiometric quantities of precipitating chemicals such as sodium carbonate, lime, iron salts, alum and sodium sulfide have been metered into the

Dynactor system successfully decontaminating water contaminated with several types of hazardous materials. Wherever possible the decontaminating chemical should be used in the powdered form to minimize logistics in the field. For example, water containing 100 ppm of lead nitrate was pumped through the Dynactor while powdered sodium bicarbonate was aerosolized into the 5 gpm continuous flowing system. Lead carbonate precipitate was immediately observed in the effluent and a filtered sample showed 2 ppm of lead by atomic absorption analysis. Most of the toxic heavy metals can be reduced to innocuous levels by precipitation and removal of a highly insoluble salt. Other precipitation reactions will be reported.

Carbon Adsorption

Because powdered carbon treatment of contaminated water is recognized effective countermeasure for the removal of about 80 percent of the hazardous chemicals of high ranking importance in the Battelle Report*, significant effort has been devoted to the perfection of a process for continuous flow carbon treatment of hazardous material contaminated waters. The powdered activated carbon studied was Nuchar-190-N produced by West Virginia Paper and Pulp Company. This carbon was chosen for the initial studies because extensive data on pesticide adsorption by Nuchar-190 was available from scientific literature. Other types and sources of activated carbon will also be studied.

Powdered activated carbon has been metered into the Dynactor as a 10 percent aqueous suspension and as a dry powder. The dry powder is the preferred method of treatment for a mobile field application. Using the powder feed mechanism designed for the Dynactor, the activated carbon is aerosolized directly into the throat of the unit making intimate contact with the thin film of flowing liquid ejected from the nozzle. The wetting and dispersion of the carbon by the turbulent thin film contact was excellent at a liquid flow rate of 4 gallons per minute and a carbon metering rate of about 15 to 20 grams per minute. The adsorption of phenol, Ethion and DDT have been extensively studied and will serve as examples to demonstrate the feasibility of the Dynactor as a continuous flow carbon treatment unit for the removal of hazardous materials from contaminated water. Initial and final concentrations of phenol were assayed by gas chromatography and the two pesticides by election capture gas chromatography after concentration by extraction in hexane. The effluent from the Dynactor was immediately filtered through a 0.45 micron Millipore filter to remove the carbon and analyzed.

The results on the adsorption of phenol are shown in Figure 4. These data were obtained using a 10 percent suspension of Nuchar-190-N metered into the Dynactor; comparable data have also been obtained using powdered Nuchar-190-N aerosolized into the unit. Adsorption of phenol from the contaminated water is achieved in less than two minutes and greater than 90 percent removal of phenol is obtained with carbon to phenol weight ratios of about 20 to one.

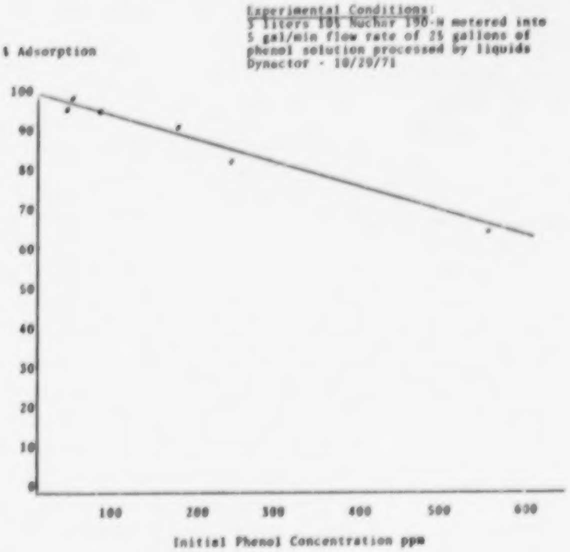

Figure 4: Phenol Adsorption Versus Initial Phenol Concentration

The results on the adsorption of Ethion are shown in Table I.

TABLE I

Adsorption of Ethion in the Dynactor System Using Powdered Activated Carbon

Initial Ethion Concentration	Final Ethion Concentration	Carbon Used	Carbon/Ethion Ratio
18 ppm	11 ppb	160 g	89
13 ppm	28 ppb	10 g	8
8.5 ppm	4 ppb	100 g	118
5 ppm	4 ppb	75 g	150
1.6 ppm	6 ppb	20 g	125

The system worked well in removing 99.9 percent of the initial concentration of Ethion present even with relatively low ratios of carbon to pesticide.

Control of Spillage of Hazardous Polluting Substances, G. W. Dawson, A. J. Shuckrow, and W. H. Swift, Battelle Memorial Institute, Program No. 1508, Contract No. 14-12-866, November 1, 1970.

The results on the adsorption of DDT are shown in Table II.

TABLE II

Initial DDT Concentration	Final DDT Concentration	Carbon Used	Carbon/DDT Ratio
2.00 ppm	17 ppb	50 g	250
1.00 ppm	0.650 ppb	70 g	700
0.445 ppm	0.485 ppb	100 g	2200
0.186 ppm	0.750 ppb	60 g	3300
0.098 ppm	0.400 ppb	60 g	6000

Greater than 99 percent of the initial DDT concentration was removed leaving negligible quantities of DDT in the effluent.

Studies on the continuous flow separation of carbon from the Dynactor effluent are still in progress. Several flocculating agents of the polyelectrolyte type have been studied. One in particular, Nalco No. 8173, was found very effective in producing a suitable floc within a few seconds' contact time. Methods to separate this floc instantly yielding a clear effluent will be reported. With the perfection of a continuous flow carbon separation method, we have demonstrated the complete feasibility of the Dynactor system to remove toxic substances from water by adsorption on carbon in a continuous flow mobile configuration.

Future Program Objectives—Mobile Decontamination Units

Phase I has successfully demonstrated the feasibility of the Dynactor/Separator System to decontaminate spilled hazardous materials in waterways in a rapid continuous flow configuration. Phase II involves scaling up of the system to process 1,000 gpm (1.4 million gallons per day) in a mobile configuration schematically shown in Figure 5. A suitable arrangement of valves and interconnections is provided so that various kinds of spills can be treated by making the proper hydraulic interconnections and connecting the appropriate reagents with the system as dictated by the reactions desired. Gases, neutralizing chemicals, precipitating chemicals or adsorbents such as activated carbon can be metered into the Dynactor either as powders, liquids or slurries to effect the desired decontamination of the spilled hazardous material. The effluent can be processed as needed to remove precipitates or flocculated carbon and the effluent returned to the waterway. A second Dynactor can be added to the line to insure maximum aeration of the final effluent if this is found to be warranted.

Two types of mobile systems are envisioned. One system would be mounted on a trailer and would contain all equipment necessary to combat a spill except for the pumps and motor. This unit is designed for use with conventional fire depart-

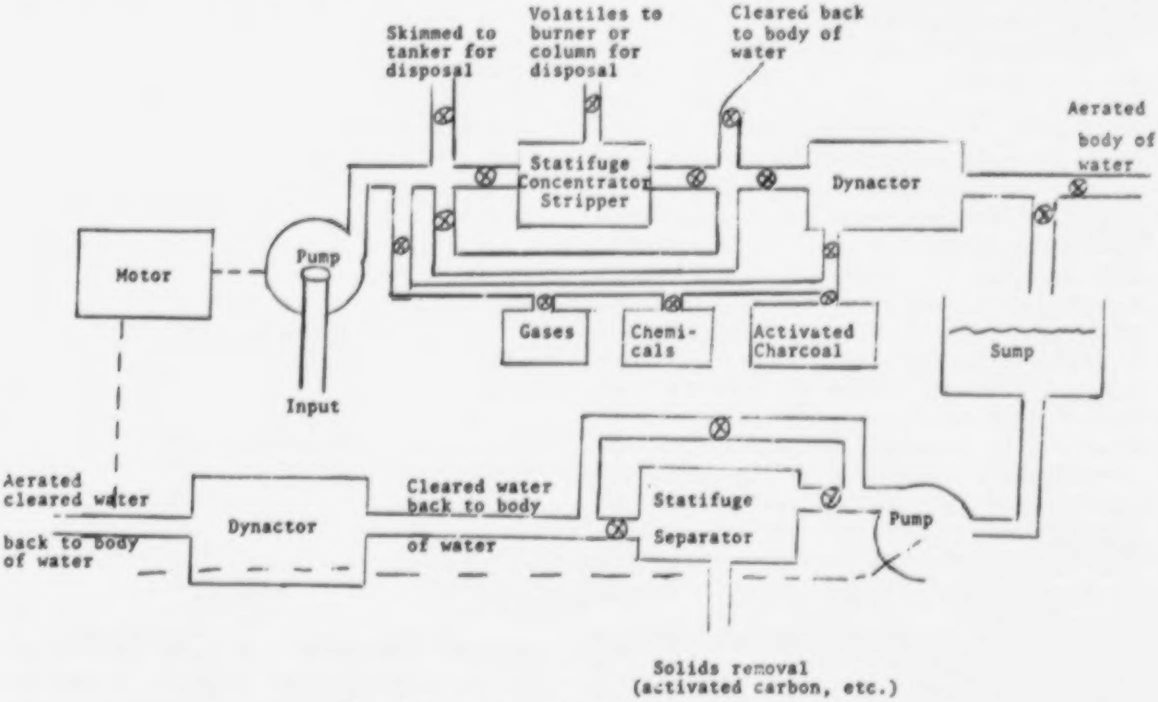
Skimmed to tanker for disposal
Volatiles to burner or column for disposal
Cleared back to body of water
Aerated body of water
Statifuge Concentrator Stripper
Dynactor
Motor
Pump
Input
Gases
Chemi-cals
Activated Charcoal
Sump
Aerated cleared water back to body of water
Dynactor
Cleared water back to body of water
Statifuge Separator
Pump
Solids removal (activated carbon, etc.)

Figure 5: Basic Scheme of Mobile Decontamination Unit

ment pumper equipment. The second type of system would be completely self-contained, including pumps and motor, which would be mounted on an amphibious trailer unit.

The first system would be designed as a piece of equipment to be used by fire departments or civil defense agencies which have pumping equipment. It would be intended for spills occurring close to roads, highways and/or railroad lines and would be designed for bodies of water accessible from a roadway with relatively short hose requirements to reach the contaminated site. The second system, which could be used every place where the first type is applicable, could also be used afloat on bodies of water where it would be impractical to employ long hoses. Generally, this would be intended for lakes, ponds and large rivers and could effectively process the hazardous material from the center of the plume of dispersion.

The ultimate objective of this program could be the creation of a fleet of decontamination vehicles stored in appropriate depots. The most needed reagents and adsorbents could be stored in the same locations. At the time of a spill the mobile decontamination unit could be sent to the scene, along with the appropriate materials required to perform the proper physical and chemical reactions to decontaminate the particular material spilled into the environment.

A MOBILE MULTIPURPOSE TREATMENT SYSTEM FOR PROCESSING HAZARDOUS MATERIAL CONTAMINATED WATERS

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INTRODUCTION

The recent concern for the accidental entrance of hazardous materials into a watercourse has initiated several programs by the Environmental Protection Agency for the control of this problem. The program described herein was undertaken to develop a transportable treatment system for on-site removal and treatment of spilled hazardous materials in aqueous solutions. This program has the following objectives:

1. Design and fabricate a mobile treatment system for spilled hazardous materials.
2. Complete a detailed laboratory investigation for treating various types of hazardous materials.

System Design Considerations

A treatment system for processing spilled hazardous materials requires a high degree of flexibility in order to adequately cope with a wide variety of substances. In addition to the actual spilled material, consideration must be given to contamination of the spilled material with soil and debris, material immediately added to the spill for safety reasons (for example, the addition of lime to acrylonitrile to prevent release of HCN gas), and substances already present in the water which has been contaminated. In cases where the spill has been confined and not diluted with water, it was assumed that the spilled material would not be processed by the treatment system, but pumped directly into shipping containers. If, however, clean-up of the area produced contaminated water, this would be processed by the treatment system.

The list of hazardous materials which was considered in selecting a treatment scheme is presented in Table I. Treatment of these materials involves water soluble inorganic materials and both water soluble and insoluble organic materials. In addition, removal of suspended materials from secondary contamination was considered. The unit processes selected to remove this wide range of contaminants includes: reaction/flocculation, sedimentation, granular media filtration, and granular activated carbon adsorption. These unit processes will remove the majority of pollutants involved in a spill with the exception of the water soluble inorganics.

A schematic flow sheet of the treatment process is presented in Figure 1. The contaminated water is pumped from the source via a submersible pump into a reaction/flocculation tank. Various treatment chemicals can be added at this point to condition the waste for further treatment. Energy for flocculation is provided via a recirculation pump. The waste then flows to a settling tank. The overflow from the settling tank is filtered through granular media filters followed by granular activated carbon adsorption. An in-line eductor type aerator provides aeration of the final effluent prior to discharge. Sludge is removed from the sedimentation tank and stored for ultimate disposal. An additional storage

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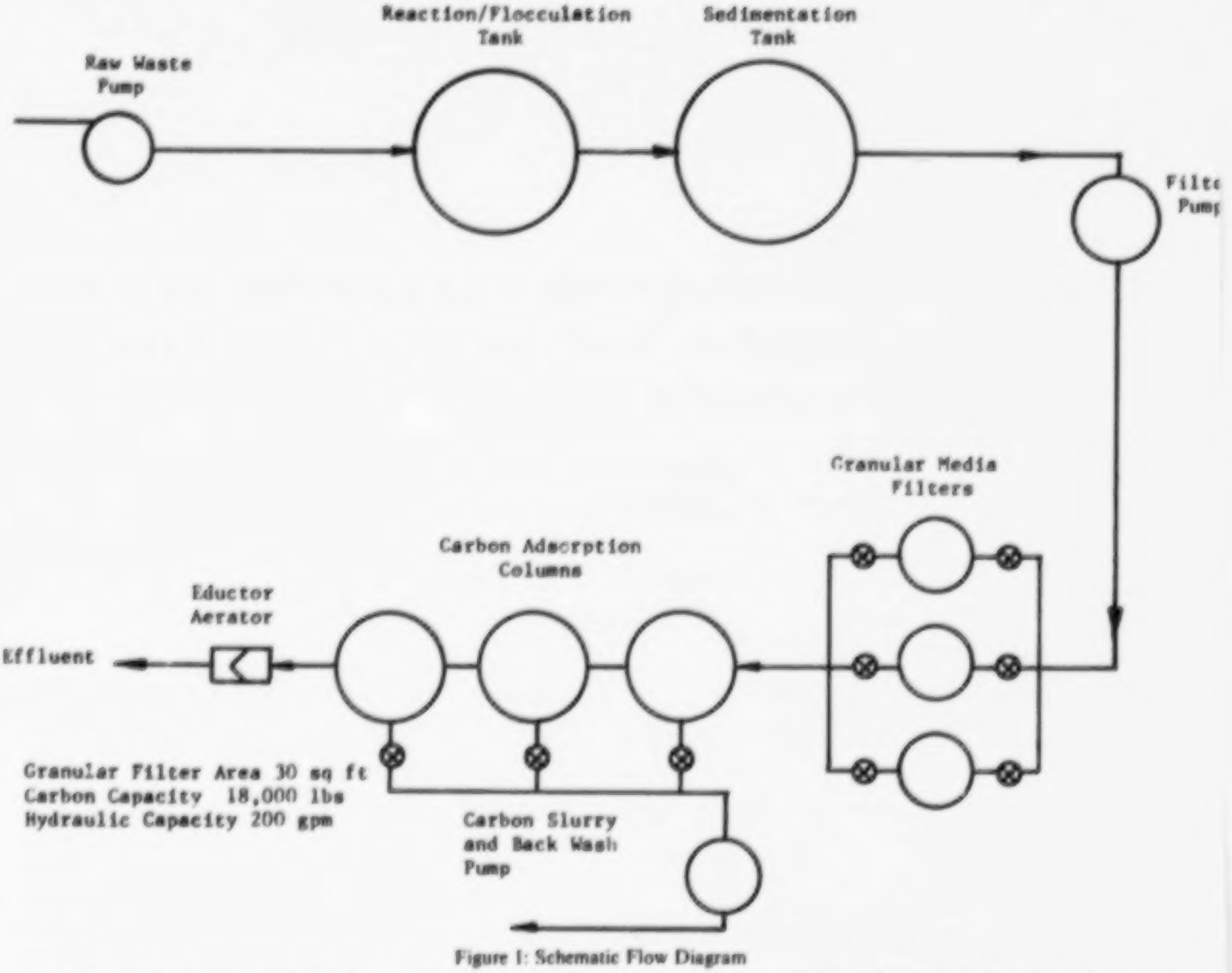
Raw Waste Pump
Reaction/Flocculation Tank
Sedimentation Tank
Filte Pum
Granular Media Filters
Carbon Adsorption Columns
Eductor Aerator
Effluent
Granular Filter Area 30 sq ft
Carbon Capacity 18,000 lbs
Hydraulic Capacity 200 gpm
Carbon Slurry and Back Wash Pump

Figure 1: Schematic Flow Diagram

tank is provided for filter backwashing operations. Each unit process may be bypassed if not required for a specific spill.

Once the system flow sheet was selected, the actual system had to be designed to meet the various limitations imposed upon transportable equipment. The most significant limitations involve size and weight. A 45 ft trailer in conjunction with a snub nose tractor met the required 55 ft total vehicle length imposed by many states. The trailer selected was of the low bed design to provide the maximum usable height for the carbon columns and filters. A specific problem was encountered in the carbon system regarding the state of the carbon during transportation. Initially, to conserve overall weight, the carbon was to be shipped dry. It was discovered, however, that a significant amount of time was required for wetting the carbon (12-48 hrs in cold water), and a means for carbon drying could not be incorporated into the system. The mode of transportation was then changed to backwashed and drained. This increased the weight of carbon considerably, since one pound of dry carbon absorbs about one pound of water. Instead of reducing treatment capacity, the total system over the road weight was increased to 105,000 pounds, which requires yearly permits in most states.

The selection of the materials of construction for the treatment system required many considerations. The list of dilute corrosives to be handled is presented in Table 1. Other design criteria used in determining the most suitable materials were the following:

1. Strength and durability
2. Weight
3. Economy
4. Availability
5. Serviceability

The maximum concentration of hazardous material in the waste was set at 1% for design purposes, and the ambient temperature range was defined as 0-

110°F. The system will be used only intermittently. After each spill is picked up, the system will be thoroughly flushed with clean water.

The types of corrosion resistant piping most commonly used in the chemical industry are metal alloy pipe, lined pipe, and plastic pipe. After much research, the following available materials stand out as suitable for this system: stainless steel, monel, alloy 20, solid polypropylene, and cast iron pipe with saran, penton, or kynar lining.

It was immediately apparent in searching for materials that no one material of any type could withstand corrosion from the entire list of spilled materials. For example, the plastics listed above could perform well on most corrosives in Table 1, but show weakness when handling solvents at higher temperature as well as questionable strength and durability in a mobile system. On the other hand, stainless steel is considered suitable for strength and high temperature performance as well as for most corrosive items except chlorinated substances. Economic considerations required the selection of a material which resists most corrosives but not necessarily all. Furthermore, the treatment system is anticipated to be utilized only intermittently and is expected to be flushed after each use.

TABLE 1

List of Hazardous Spilled Materials

Contract List

1. anhydrous ammonia
2. phenol
3. chlorine: saturated chlorine water
4. acrylonitrile
5. acetone cyanohydrin
6. methyl alcohol
7. tetraethyl lead
8. tetramethyl lead
9. chlorinated hydrocarbon pesticides

Additional Priority Ranking Materials Considered

10. chlorosulfonic acid:
    hydrochloric acid
    sulfuric acid
11. benzene
12. phosphorus pentasulfide
13. styrene
14. nonyl phenol
15. nitrophenol
16. isoprene
17. ammonium nitrate
18. aluminum sulfate

A comparison of the estimated prices and weights for various materials was made. Stainless steel type 304 was the lowest priced material, but was not recommended because of its lower resistance to various corrosives compared to stainless steel type 316. All other materials except solid polypropylene and stainless steel type 316 were considered either too expensive or high in weight and were eliminated from consideration. Solid polypropylene was found to be competitive with type 316 stainless steel and also offered a significant advantage in weight. However, its strength, durability and resistance to vibrational damage due to the mobility of the treatment system were questionable. A number of inquiries were made to find an installation of solid polypropylene pipe system that could demonstrate this material's ruggedness. However, no satisfactory installation could be found. On the other hand, the strength and durability of stainless steel type 316 are well proven in the chemical field. Therefore, stainless steel type 316 was utilized as the construction material for the pipes and fittings.

The Treatment System

The entire treatment system is transported in a low-bed 45 ft trailer. The pumps, generator, filters, carbon columns and plumbing are rigidly mounted to the trailer bed. The reaction/flocculation, sedimentation, sludge storage and back wash storage tanks are of the collapsible type, and are erected at each treatment location. A pictorial sketch is presented in Figure 2 depicting the unit in operation, while Figure 3 presents a sketch of the inside of the trailer module.

Laboratory Investigations

In order to adequately define the treatment capabilities of the mobile treatment system, a detailed laboratory study is being performed concurrently with design and construction of the treatment unit. Areas being investigated include chemical treatment requirements, carbon adsorption capacity, nature and quantities of residual sludges and other process requirements.

The laboratory investigations also include determination of the feasibility of utilizing reverse osmosis (RO) for processing spilled hazardous materials. Recent advances in RO technology have provided a chemically stable aromatic-polyamide membrane which can be operated over a wide pH range. A potential advantage of RO treatment is the ability to concentrate the spilled hazardous material. Concentrations as high as ten-fold can be obtained and possibly higher depending upon the solubility of the material being concentrated. The concentrated product could then be transported from the spill site for by-product recovery or additional treatment. The newer RO systems utilizing the hollow fiber concept are very compact and well adapted to mobile treatment units.

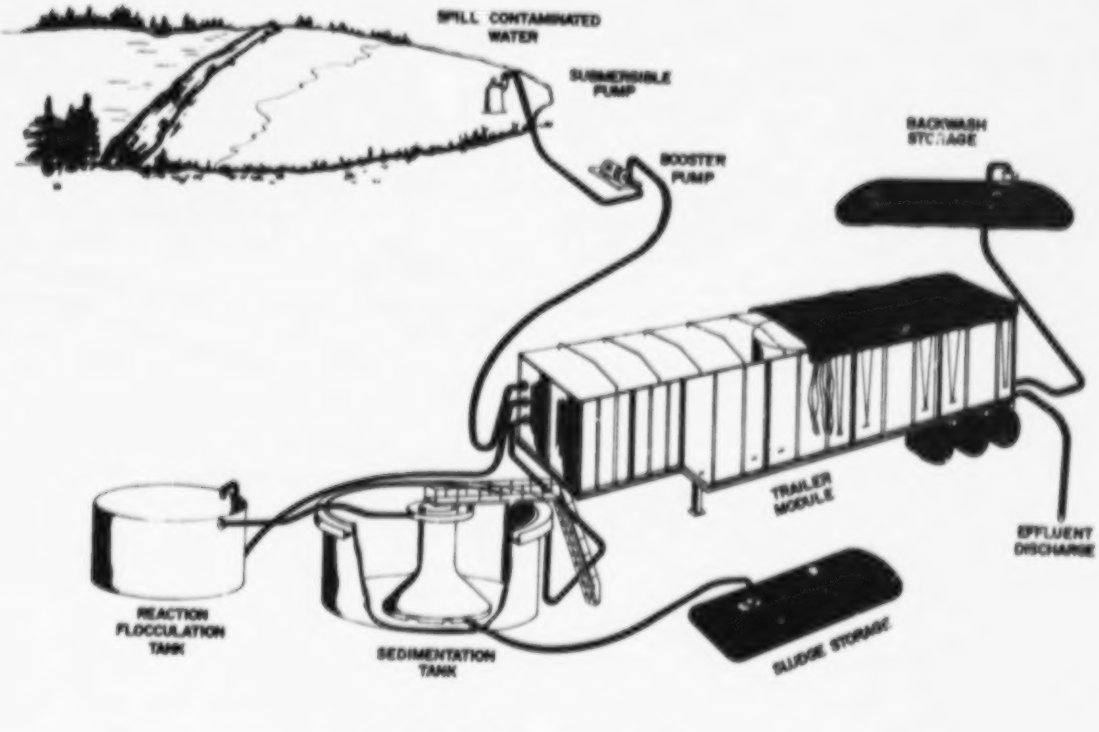

Figure 2: System Arrangement

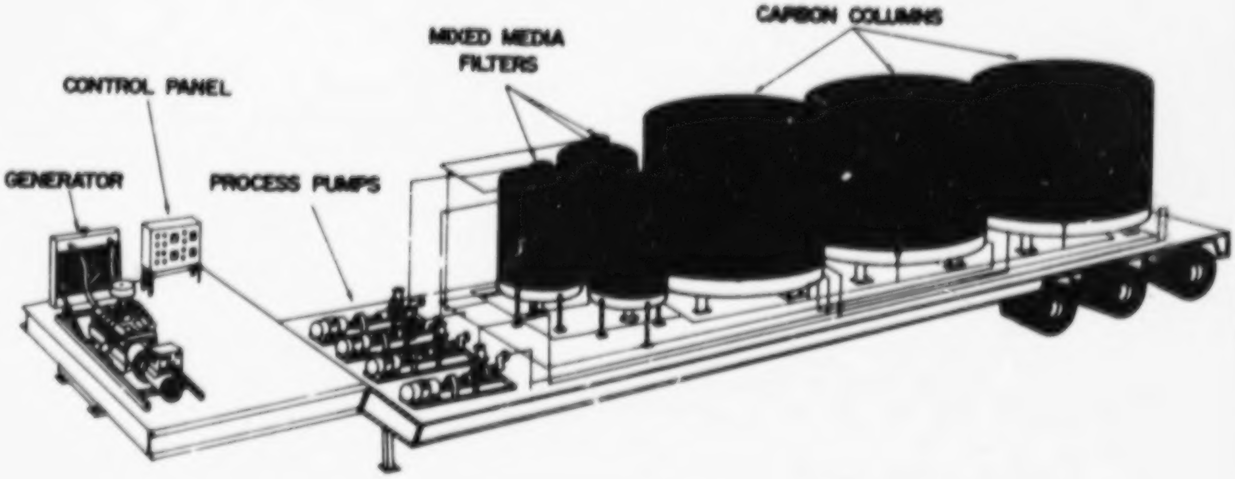

Figure 3: Trailer Module Arrangement

IN SITU TREATMENT METHODS FOR HAZARDOUS MATERIAL SPILLS*

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and
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Environmental Protection Agency

ABSTRACT

Several methods for coping with water and land spills of hazardous materials are discussed. For water spills of heavy metals, treatment with sodium sulfide to form a sulfide precipitate is described. Laboratory and field data are presented which illustrate the general utility of this method. Methods are suggested for neutralizing spills of ammonia and chlorine. For treating water spills of certain organic pollutants and heavy metal salts, adsorption by activated carbon is shown to be promising. Data are presented on the effects of pollutant concentration on carbon adsorption efficiency. Flotation techniques for retrieving powdered activated carbon from the treated water are described, and the use of granular activated carbon in porous bags is considered as a means for overcoming the disadvantages of introducing carbon directly into the bulk water. Methods are available for controlling land spills of hazardous materials by treating the ground surface to prevent penetration and by gelling or congealing spilled liquids to immobilize them.

INTRODUCTION

Both land and water spills of hazardous materials present potential threats to the environment. Therefore, it is imperative that effective means be available for coping with such spills under a variety of circumstances.

Under sponsorship of the Environmental Protection Agency, Office of Research and Monitoring, the Cornell Aeronautical Laboratory, Inc. (CAL) is investigating methods for treating, controlling, and monitoring hazardous materials spills. Priority is being given to those materials which are manufactured and shipped in large quantities, and which pose an imminent threat to the environment if spilled. Specific chemicals included in the study are: anhydrous ammonia, chlorine, phenol, acrylonitrile, acetone cyanohydrin, methyl alcohol, and water-soluble heavy metal salts. As appropriate treatment methods are developed for these chemicals, the techniques will be extended to other hazardous substances which are also produced and shipped in large quantities.

Methods under investigation for treating water spills include adsorption on activated carbon, precipitation of heavy metals by the addition of sodium sulfide, and neutralization. Methods for coping with land spills include treatment of the soil surface to prevent percolation, and means for gelling, congealing, or polymerizing the spilled material to render it immobile. In all cases, consideration will be given to logistic and cost factors. Also, bioassays are being performed for each of the proposed treatment methods to insure that the treatments themselves are not detrimental to aquatic organisms. The program also includes the development of detection and monitoring techniques. The present paper is concerned with *in situ* treatment methods for land and water spills. Detection and monitoring were discussed at this conference in an earlier paper by D. Bock and P. Sullivan.

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*Work sponsored by the Environmental Protection Agency under Contract No. 68-01-0110.

Activated Carbon Treatment

Adsorption by activated carbon has been used successfully for purifying water for many years. The method is usually applied in closed treatment systems where the activated carbon is used as part of the filtration process. In the present case, we are considering the use of activated carbon in open watercourses. Clearly, the use of activated carbon under such circumstances presents many problems not encountered in confined systems. In order to evaluate the feasibility of applying carbon adsorption as a means for treating spills in open watercourses, it is necessary to measure the adsorption efficiency of activated carbon for the pollutants of interest and to investigate means for disseminating carbon in the spill area and later, retrieving it. Under the present program, laboratory experiments are being conducted to determine the amount of each pollutant adsorbed by various types of activated carbon for different pollutant concentrations. Air flotation is being studied as a possible means for removing the activated carbon from the water after the treatment is complete. An alternative treatment technique under study is to introduce the carbon into the water in porous bags which allow the polluted water to enter the bag freely and interact with the carbon particles. Since the carbon particles are confined to the bags, removal subsequent to treatment is a simple matter.

Carbon adsorption experiments have been performed on phenol, acetone cyanohydrin, acrylonitrile, methanol, and a number of heavy metal compounds. The test procedure consists of preparing one hundred-milliliter samples of the pollutant at various concentrations and adding activated carbon over a range of dosages. Individual sample bottles containing the test solutions are then placed on a continuously-operating tumbler for selected time periods. Upon removal from the tumbler, the sample solutions are filtered through a No. 3 Whatman filter paper and the filtrate is analyzed to determine the residual concentration of the pollutant. The filtrate is analyzed by spectral photometry, gas chromatography, or atomic absorption spectroscopy as appropriate. For all of the carbon adsorption tests described below, whenever contact (or tumbling) times are not explicitly stated, it can be assumed that contact times were sufficiently long that the adsorption data correspond very nearly to ultimate adsorption capacities.

Tests on the adsorption of phenol on Aqua Nuchar A powdered activated carbon were made for initial phenol concentrations ranging from 50 ppm to 1,000 ppm, and carbon dosages ranging from 100 ppm to 10,000 ppm. The concentration of phenol in the filtrate was determined by measuring optical absorptivity at a wavelength of 270 millimicrons. The data plotted in Figure 1 indicate that carbon adsorption is a fairly effective means for treating spills of phenol. Figure 2 shows the weight of carbon required per weight of phenol spill to effect a specified percentage of phenol removal for five different

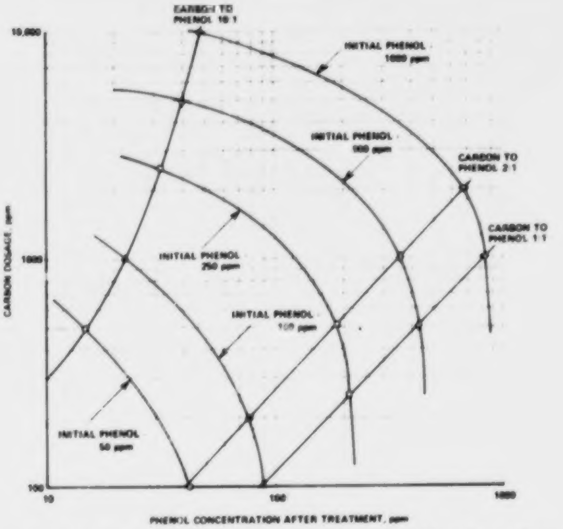

Figure 1: Residual Phenol Concentrations Resulting from Powdered Carbon Dosages (Aqua Nuchar A)

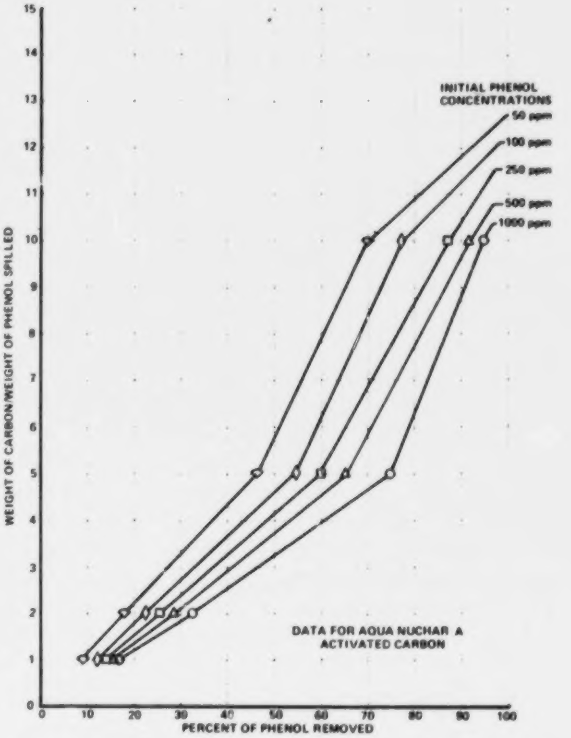

Figure 2: Weight of Carbon Required Per Unit Weight of Phenol Spilled as a Function of Percent Removal

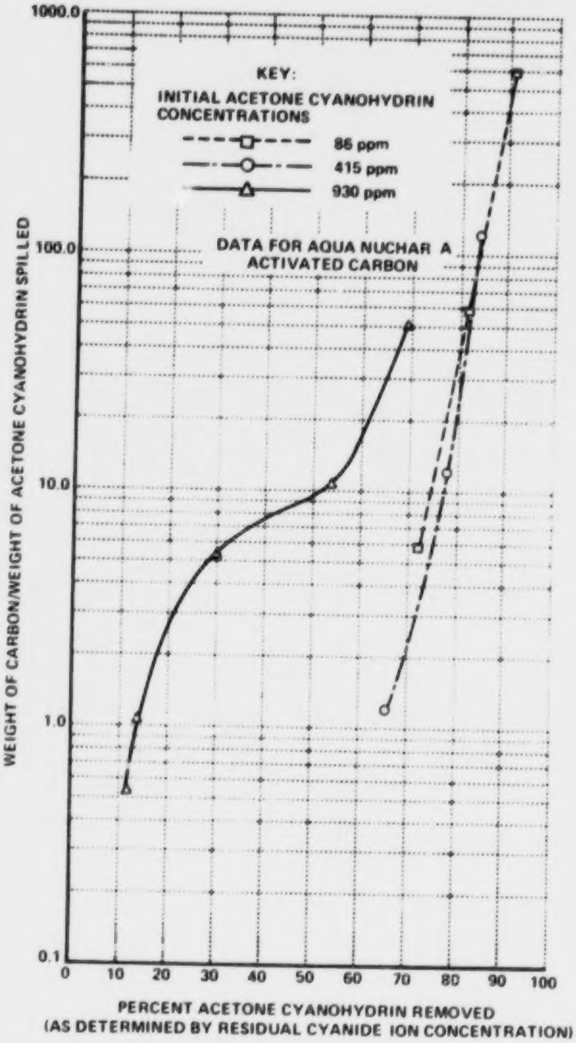

Figure 3: Weight of Carbon Required per Unit Weight of Acetone Cyanohydrin as a Function of Percent Removal

initial concentration levels of phenol. This figure indicates that, for a spill of 1,000 pounds of phenol, approximately 4,800 pounds of carbon would be required to effect a removal of 70%, provided that treatment was initiated when the phenol concentration in the water was 1,000 ppm. This figure graphically illustrates the need for a rapid response to a spill situation. If treatment is delayed until the average phenol concentration is reduced to 50 ppm, 10,000 pounds of carbon would be required to effect a 70% removal of the initial 1,000 pound spill.

Carbon adsorption tests for acetone cyanohydrin were also made using Aqua Nuchar A powdered activated carbon. Acetone cyanohydrin is highly soluble in water and decomposes into acetone and hydrogen cyanide. Therefore, following carbon treatment, the filtered solutions were analyzed for cyanide ion concentration using a specific ion electrode. Results of these tests are shown in Figure 3 where the percent removal is based on measurement of the residual cyanide ion concentration rather than on direct determinations of acetone cyanohydrin depletion. Initial concentrations of acetone cyanohydrin of 930 ppm, 415 ppm, and 86 ppm were used. The effectiveness of carbon treatment measured in terms of the weight of carbon required per unit weight of acetone cyanohydrin is nearly the same for concentrations of 415 ppm and 86 ppm. The data show that, for a 70% removal of the pollutant at the lower concentration levels, approximately three pounds of carbon would be required per pound of pollutant. On the other hand, for a concentration of 930 ppm, approximately 50 pounds of carbon would be required to effect the same percent removal. Considering the carbon requirements only, the data suggest that the carbon is used more efficiently if one waits for the spill to dilute. Other considerations, such as the difficulty in coping with a larger spill area and the fact that a larger segment of the aquatic environment would be affected, would dictate that rapid response and treatment are preferred.

For acrylonitrile adsorption tests, the filtrate was analyzed by means of gas chromatography. The results of adsorption tests for acrylonitrile using Aqua Nuchar A powdered carbon are presented in Figure 4. For initial pollutant concentrations of 1,000 ppm and carbon-to-acrylonitrile doses of 1:1 (by weight), the adsorption efficiency is comparable to that obtained in the case of phenol (Figure 1). However, as the carbon dise is increased from 1:1 to 10:1, the residual acrylonitrile concentration decreases from approximately 880 ppm to 480 ppm. This reduction is considerably less than in the case of phenol, where a 10:1 dosage of carbon at 1,000 ppm initial pollutant concentration resulted in a residual phenol concentration of approximately 40 ppm. In other words, for initial concentrations of 1,000 ppm, a 50% reduction in the acrylonitrile requires ten pounds of carbon for every pound of acrylonitrile spilled, whereas in the case of phenol, a 50% removal can be achieved by slightly more than three pounds of carbon per pound of phenol spilled.

For methyl alcohol, which is highly soluble in water, removal by carbon adsorption is highly ineffective as would be expected. Results of carbon adsorption tests using Aqua Nuchar A are presented in Table I. A carbon-to-methyl alcohol weight ratio of 13 results in a removal of only 17%. For a removal efficiency of 73%, a carbon-to-pollutant weight ratio in excess of 6,600 is required. Carbon adsorption is not an efficient method for treating spills of methyl alcohol.

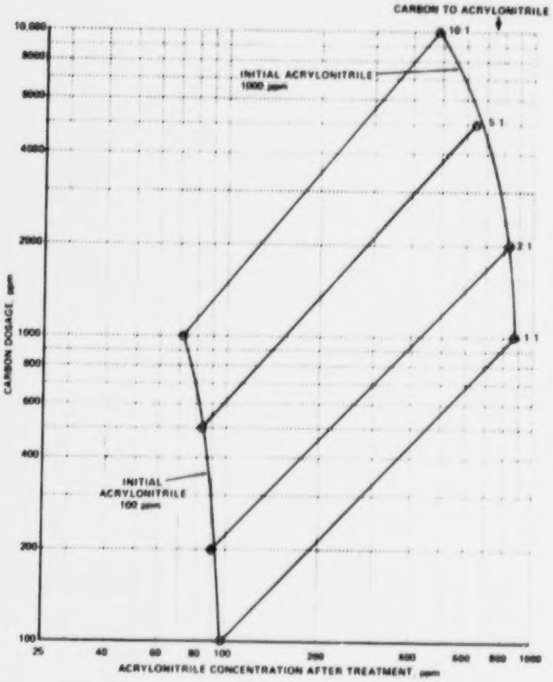

Figure 4: Residual Acrylonitrile Concentrations Resulting from Powdered Carbon (Aqua Nuchar A) Treatment

TABLE 1

Influence of Initial Methyl Alcohol Concentration on Adsorption by Activated Carbon*

Initial CH_3OH Concentration (ppm)	Residual CH_3OH Concentration (ppm)	Percent Removal
770	640	17
154	103	33
15	10	33
1.5	0.4	73

*Carbon dosage = 10,000 ppm Aqua Nuchar A

For spills of certain heavy metal compounds in watercourses, adsorption by activated carbon is potentially an effective means for removing the heavy metals from solution. Experiments were conducted on lead, manganese, copper, nickel, chromium, and mercury salts. Of the heavy metal compounds tested, carbon adsorption efficiency was highest for those containing lead and mercury. Results of experiments conducted using lead acetate at a lead concentration of 120 ppm and a range of doses of Aqua Nuchar C-190N are presented in Table II. At a carbon-to-lead ratio (by weight) slightly greater than four, over 59% of the lead was adsorbed. Lead adsorption experiments were also conducted using lead nitrate solution. The results in Table III indicate that for an initial lead concentration of 107 ppm and a carbon-to-lead weight ratio of about five, only 13% of the lead is removed. It was expected that the lead removal from a lead nitrate system would be lower than that from a lead acetate system, because nitrate is an inorganic anion while acetate is an organic anion.

TABLE 2

Effect of Activated Carbon Concentration: Lead Acetate System*

Activated Carbon Concentration** ppm	Residual Lead Concentration ppm	Percent Removal of Lead
0	120.0	0
500	49.0	59.1
1,000	43.0	64.2
10,000	10.5	91.2

*Initial lead concentration = 120 ppm
**Aqua Nuchar C-190N
Initial pH = 5.4

Comparison of Tables II and III indicates that the lead removal for the lead nitrate system was generally lower; however, at carbon-to-lead weight ratios of about 100:1, the percent removal exceeded 90% for both the lead acetate and the lead nitrate systems.

TABLE 3

Effect of Activated Carbon Concentration: Lead Nitrate System

Activated Carbon Concentration** ppm	Residual Lead Concentration ppm	Percent Removal of Lead
0	107*	0
500	93	13
1,000	88	17.7
5,000	17	84
10,000	7.5	93

*Initial lead concentration = 107 ppm
**Aqua Nuchar C-190N
Initial pH = 4.65
No pH adjustment

For the lead experiments discussed above, distilled water was used. Additional experiments on lead adsorption by carbon were conducted using water obtained from a local creek. The results for lead acetate are shown in Table IV at initial lead concentrations of 100 ppm and carbon dosages of 10,000 ppm of Nuchar C-190N powdered activated

TABLE 4

Removal of Lead from Distilled Water Solution and from Creek Water Solution (Contact Time Study)*

Water	Contact Time Minutes	Residual Lead Concentration ppm	Percent Removal
Distilled Water	0	100	0
Distilled Water	10	6	94
Distilled Water	30	6	94
Distilled Water	80	6	94
Distilled Water	180	6	94
Creek Water	0	100	0
Creek Water	10	6.4	93.6
Creek Water	30	6.4	93.6
Creek Water	80	6.4	93.6
Creek Water	180	6.4	93.6

Notes:
*No pH adjustment
Carbon dosages = 10,000 ppm NUCHAR C-190N
Initial lead concentration = 100 ppm
Lead compound = lead acetate

carbon. Comparison of the results for distilled water and creek water show little difference in lead removal. However, markedly different results for distilled and creek water were obtained when lead nitrate was used. The results of the lead nitrate experiments are presented in Table V for initial lead concentrations of about 100 ppm for both distilled water and creek water, and carbon dosages ranging from 500 to 10,000 ppm. In the case of creek water, for carbon dosages of 500 ppm or more, greater than 96% of the lead was removed. Of special significance is the fact that at zero carbon dosage for creek water, 69% of the lead was removed. The experimental procedure used for the lead experiments was very similar to that used for the other materials discussed previously. After treatment with carbon and tumbling, the solution was filtered through a No. 3 Whatman filterpaper. The residual lead in the filtrate was measured by atomic absorption spectroscopy. For the lead nitrate system, the 69% removal of lead with no carbon treatment indicated that a precipitate was formed in the creek water and that the precipitate was removed upon filtration. The significance of the result presented in Table V is that a substantial reduction in lead content in the bulk water of a stream can occur through natural precipitation.

The results of experiments on other heavy metals using various compounds are presented in Table VI. For each of the indicated heavy metals, the specific compounds used for the experiment are indicated. Carbon-to-heavy metal ratios as high as 100:1, and in one case, 200:1, were used. Of the various metals tested, mercury showed the highest affinity for activated carbon. A carbon-to-mercury dose of five by weight effected greater than 99% removal of the mercury.

TABLE 5

Removal of Lead from Distilled Water Solution and from Creek Water Solution (Carbon Dosage Study)*

Water	Activated Carbon Dosage ppm	Residual Lead Concentration ppm	Percent Removal ppm
Distilled Water	0	107	0
Distilled Water	500	93	13
Distilled Water	1,000	88	17.7
Distilled Water	5,000	17	84
Distilled Water	10,000	7.5	93
Creek Water	0	31.0	69.0
Creek Water	500	3.4	96.6
Creek Water	1,000	3.4	96.6
Creek Water	5,000	3.4	96.6
Creek Water	10,000	3.4	96.6

Notes:
*No pH adjustment
Contact time = 60 minutes
Lead compound = lead nitrate
Activated carbon = NUCHAR C-190N
Initial lead concentration:
Distilled water system = 107 ppm
Creek water system = 100 ppm

Carbon Flotation

In the activated carbon experiments discussed above, the activated carbon was mixed directly into the pollutant-water solution. In a spill situation in the real world, dumping activated carbon into streams and lakes as a treatment method at some of the dosages considered above (e.g., 5,000 to 10,000 ppm) causes a severe blackening of the water. Thus, from a purely esthetic point of view, this treatment method is in itself undesirable. However, carbon treatment might be acceptable if suitable means can be found to remove most of the carbon following spill treatment, or, if it can be shown that the pollutant-laden carbon, after settling to the bottom of the watercourse, will not have an adverse effect on the aquatic environment. Desorption of the pollutant from the settled carbon may occur eventually, but if the rate of desorption is low enough, pollutant centrations in the bulk water might be reduced to acceptable levels. However, until the long-term effects on the aquatic environment can be evaluated fully, it is desirable that means be found for pre-

TABLE 6

Carbon Adsorption of Mn, Cu, Ni, Cr, and Hg

Heavy Metal Tested	Activated Carbon Dosage ppm	Residual* Metal Concentration ppm	Percent Removal
Mn	0	100	0
Mn	500	99	1
Mn	1,000	97	3
Mn	5,000	75	25
Mn	10,000	50	50
Cu	0	50	0
Cu	500	46	8
Cu	1,000	45	10
Cu	5,000	13.5	73
Cu	10,000	1.8	96.4
Ni	0	100	0
Ni	500	96	4
Ni	1,000	95	5
Ni	5,000	89.5	10.5
Ni	10,000	48	52
Cr^{+6}	0	100	0
Cr^{+6}	500	84	16
Cr^{+6}	1,000	74	26
Cr^{+6}	5,000	66	34
Cr^{+6}	10,000	64	36
Hg	0	100	0
Hg	500	<1	>99
Hg	1,000	<1	>99
Hg	5,000	<1	>99
Hg	10,000	<1	>99
Cr^{+3}	0	100	0
Cr^{+3}	500	95	5
Cr^{+3}	1,000	92.5	7.5
Cr^{+3}	5,000	82.5	17.5
Cr^{+3}	10,000	52.5	47.5

Note:
No pH adjustment
*Initial concentrations: Mn = 100 ppm ($MnCl_2$ - 4 H_2O)
Cu = 50 ppm ($CuSO_4$)
Ni = 100 ppm ($NiCl_2$ - 6 H_2O)
Cr^{+6} = 100 ppm ($K_2Cr_2O_7$)
Hg = 100 ppm ($HgCl_2$)
Cr^{+3} = 100 ppm ($CrCl_3$ - 6 H_2O)

venting the carbon from remaining in the water for long periods of time. Therefore, methods for floating carbon particles were investigated. In these investigations, emphasis was placed on air flotation techniques whereby flotation is achieved by attachment of the carbon particles to air bubbles.

The initial laboratory studies of flotation of carbon were conducted in a cylindrical column six centimeters in diameter and 53 centimeters high fitted to a fritted glass Buchner funnel. The fritted glass funnel was of medium porosity to insure small air bubble size and uniform dispersion of bubbles. Compressed air was introduced through the end of the funnel at flow rates ranging from 2 to 8 cu ft/hr. The general setup is shown in Figure 5. Collecting agents tested were trimethyldodecylammonium chloride (Arquad 12-50), dimethyldi (hydrogenated-tallow) ammonium chloride (Arquad 2HT-75), and Cetol. The collector causes the small air bubbles produced by the fritted disc to be attached to the carbon particles, thus causing the carbon particles to float. The air-particle mixture, upon reaching the surface, forms a foam which can be removed by skimming or suction techniques.

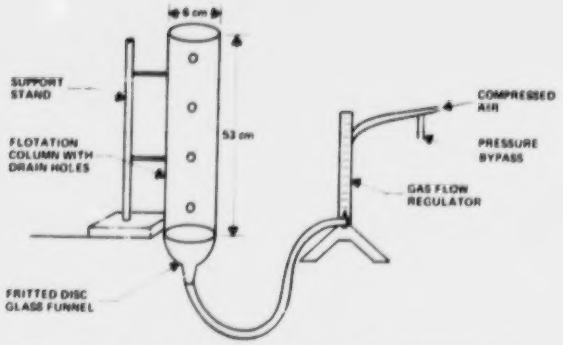

Figure 5: Apparatus for Laboratory Flotation Experiments

The amount of carbon collected with the foam is a function of collector dosage, air flow rates, and initial carbon concentration. For the laboratory experiments in the six centimeter diameter cylindrical column, the desired carbon and collector dosages were mixed with one liter of water and poured into the flotation column. The results of the flotation column experiments for Arquad 12-50 are shown in Table VII. The final volumes indicated are those of the liquid in the flotation column after the foam had been removed from the flotation column. The data show that for a carbon reduction of greater than 80%, the collector dosage must be approximately 1/10 of the activated carbon dosage.

Following the flotation experiments using carbon alone, additional flotation experiments were conducted using phenol solutions which had been treated with activated carbon. For an initial phenol concentration of 1,000 ppm and a carbon dosage of 10,000 ppm, the effects of various increments of Arquad 12-50 collector on carbon removal are shown in Table VIII. After the addition of each increment of collector and establishment of equilibrium, samples were withdrawn for analysis of residual phenol, residual carbon, and residual collector. It is evident from the table that the addition of collector causes the residual phenol concentration to increase slightly, indicating that the adsorbed phenol is displaced slightly by the collector. Comparison of Tables VII and VIII shows that the collector dosage required for carbon flotation in the carbon-phenol-water system was significantly less than in the carbon-water system. It appears that the phenol itself is acting as a collecting and flotation agent. It was also observed that a gas flow rate of only 2 cu ft/hr was sufficient for foaming in the carbon-phenol-water system, whereas a gas flow rate of 6 cu ft/hr was generally required in the carbon-water system.

On the basis of the above flotation data, it appears that the removal of a high percentage of carbon from a water system after treatment requires large amounts of collecting agent and large gas volumes. Considering a spill of 1,000 pounds of phenol and assuming that treatment will occur when the concentration is reduced to 1,000 ppm of phenol in the water, it can be determined from Figure 2 that 10,000 pounds of carbon would be required to adsorb 95% of the phenol. Now, from the data in Table VIII, which correspond to a 10:1 carbon-to-phenol weight ratio, 390 pounds of collecting agent would be required to remove all but 16 pounds of the carbon. Since the effect of a collecting agent is to displace some of the phenol, the phenol removal would be slightly less than 95%. It must be realized that the data presented in Table VIII correspond to ideal laboratory conditions. In a practical field situation, it is expected that this efficiency would be reduced considerably. From a logistics point of view, it also must be realized that to obtain the required air supply in real world conditions would be extremely difficult. Let us consider an example: Assume that phenol spilled into a stream has been treated with activated carbon and that downstream from the point of treatment, air flotation is to be attempted. Assume further that the stream is 100 feet wide and has a velocity of 0.5 ft/sec. On the basis of laboratory data, it is estimated that the carbon and the collector agent must be subjected to air bubbles continuously for at least three minutes to achieve adequate flotation. Then, the air bubble system must provide a continuous curtain of air for a distance of 90 feet along the direction of stream flow. That is, it must supply air bubbles continuously over an area 90 x 100 feet or 9,000 square feet. Laboratory experiments indicate that the minimum flow rate required to achieve flotation in the six centimeter diameter air flotation column is 2 cu ft/hr. This corresponds to a flow rate of 1 cu ft of air per minute per square foot of area. Therefore, for the case just considered, an air supply of 9,000 cu ft per minute would be required to achieve flotation of the phenol-laden carbon. This value represents an extremely large compressor system, and the logistics of installing a continuous air system of such magnitude into a stream on short notice would be extremely difficult to handle. Consequently, alternative methods for treating spills with carbon have been considered. These include the attachment of carbon particles to floating beads, the use of floating granular carbon, and the use of water-permeable recoverable bags containing the activated carbon. This latter method is discussed in further detail in the following section.

Carbon Bags

An alternative to dumping powdered or granular carbon directly into the stream with the intent of

TABLE 7

Flotation of Activated Carbon Using Arquad 12-50

(TRIMETHYLDODECYLAMMONIUM CHLORIDE, 50% ACTIVE)

TEST NO	ACTIVATED CARBON CONCENTRATION (mg/ℓ)	pH	COLLECTOR DOSAGE (mg/ℓ)	GAS RATE (CFH)	INITIAL VOLUME (mℓ)	FINAL VOLUME (mℓ)	RESIDUAL CARBON CONCENTRATION (mg/ℓ)	% REDUCTION IN CARBON CONCENTRATION	RESIDUAL COLLECTOR CONCENTRATION (mg/ℓ)	% REDUCTION IN COLLECTOR CONCENTRATION
1	5000	5.9	200	3	1000	1000	5000	0	200	0
2	5000	5.9	200	6	1000	1000	5000	0	200	0
3	5000	5.9	200	8	1000	1000	5000	0	200	0
4	5000	5.9	300	3	1030	1030	5000	0	300	0
5	5000	5.9	300	6	1030	1030	5000	0	300	0
6	5000	5.9	300	8	1030	1030	5000	0	300	0
7	5000	5.9	400	3	1060	912	2250	55	18.6	95
8	5000	5.9	400	6	1060	912	2250	55	18.6	95
9	5000	5.9	400	8	1060	912	2250	55	18.6	95
10	5000	5.9	500	3	1030	818	570	89	140	97
11	5000	5.9	500	6	890	578	175	97	9.3	98
12	5000	5.9	500	8	1030	578	175	97	9.3	98
13	5000	5.9	450	6	1070	686	370	93	86.0	80
14	5000	10.0	450	6	1020	1020	5000	0	450	0
15	5000	10.0	450	8	1020	1020	5000	0	450	0
16	5000	7.8	450	6	1020	1020	5000	0	450	0
17	5000	7.8	450	8	1020	1020	5000	0	450	0
18	5000	2.9	450	6	1020	~ 1020	>3000	–	79.0	82
19	1000	5.9	90	6	1000	690	165	84	NOT DETERMINED	–
20	10,000	5.9	900	6	1000	348	187	98	60.5	93

TABLE 8

Flotation of Activated Carbon and Adsorbed Phenol*

Collector** Concentration ppm	Residual Phenol Concentration ppm	Residual Carbon Concentration ppm	Residual Collector Concentration ppm
0	40	10,000	0
260	52	2,000	3
390	66	16	380
460		Overdose, no liquid	

*Initial phenol conc. 1,000 mg/l
carbon dosage 10,000 mg/l
**Collector, Arquad 12-50

later recovery is to introduce carbon into the stream in water-permeable bags which would allow the pollutant-laden water to pass through the bag material and interact with the contained carbon. Such bags could be attached to floats to permit them to be suspended at desired depths in the water. After treatment of the spill is complete, the bags could be easily retrieved from boats, since the floats would allow their locations to be readily determined. Tests are currently underway on bag design; however, a few desirable features are obvious. First, the bag material should be as permeable as possible to allow free exchange of water in and out of the bags. However, there is a limitation to mesh size, since if the mesh is too large, carbon will be lost from the bags. Using large carbon particles is generally undesirable because, for a given weight of carbon, greater active surface area is available with smaller particles. Thus, the porosity of the bag must be consistent with free interchange of water and ability to retain carbon. Large bags which would lump the carbon inside are undesirable because the carbon particles at the center of the "lumps" could not interact as freely with the pollutant-laden water. The bags should be thin and at the same time large in surface area. A large bag having many small pockets might be a desirable compromise.

It does not appear practical to use the bags as a "dam" which would require the water to pass through the individual bags since contact times would be too short to achieve sufficient adsorption of the pollutant. Under real world conditions, contact times on the order of tens of minutes would be required. Furthermore, the resistance of flow through the bags would create large tension on the supporting cables, and on the bags themselves. A more practical approach to the use of carbon bags would be to allow them to float along with the spill. This would greatly increase the contact time. As the spill, and therefore the bags, disperse, additional bags could be added to fill in the voids and to promote the effective pickup of the pollutant. In this intended use, however, since the bag is moving with the spill, there would be less interchange of water in and out of the bag than if the bags were held fixed. A factor of importance is the bag size relative to the turbulent cell structure of the stream.

Initial investigations of the carbon bag approach consisted of fabricating bags of different cloth types containing different kinds of carbons and studying the adsorption efficiency for phenol as a function of time of interaction. The bag sizes were two inches by three inches, and the mesh size varied from 0.8 mm x 0.5 mm to 0.25 mm x 0.3 mm. These mesh sizes did not permit the retention of powdered activated carbon, so granular carbons of various mesh sizes were used. The carbons used were Darco 8X35 mesh, Filtrasorb 300 (effective particle size 0.8 to 0.9 mm), Filtrasorb 400 (effective particle size 0.9 to 1.1 mm), Nuchar 8X30 mesh (effective particle size 0.85 to 1.05 mm), and Nuchar 20X50 mesh (effective particle size 0.35 to 0.45 mm). Data on the effective particle size of Darco 8X35 mesh were not available.

For each test, two grams of carbon were placed in a bag which was then immersed in 200 ml of a 1,000 ppm phenol solution. This carbon dosage corresponds to a concentration of 10,000 ppm. All samples were attached to a tumbler to allow uniform mixing at contact times ranging from ten minutes to three hours. The results of a number of these tests are presented in Figure 6 where "coarse bag" corresponds to a mesh 0.8 mm x 0.5 mm and both the "fine" and "medium" bags have a mesh size of 0.25 mm x 0.3 mm, but the fibers in the fine bag were heavier and tighter than those in the medium bag. The results in Figure 6 indicate that Nuchar 20X50 in a coarse bag is the most effective of the configurations tested. After about sixty minutes of contact time, the maximum adsorptive

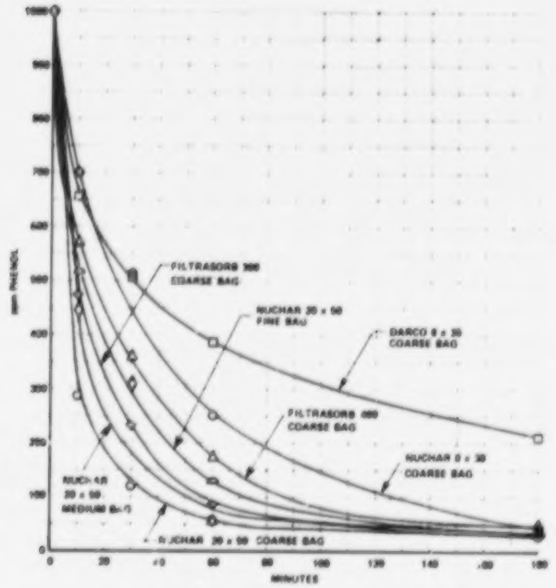

Figure 6. Bag Tests with Various Granular Carbons

capacity of the carbon is approached, leaving only about 5% of the phenol remaining in the bulk water. One can expect rather good mixing conditions in the laboratory experiments because of the tumble-type mixer that was used. It is expected that in a real stream a longer contact time would be required to achieve the same adsorptive effectiveness. Plans are now underway to test various types of carbons and bags in a stream flow facility which will permit the turbulence conditions of real streams to be simulated.

In summary, activated carbon appears to be a useful means for treating spills in streams, provided that the carbon can be removed or that it can be shown that allowing the carbon to remain in the waters will not adversely affect the environment. While generally large doses of carbon are required to effect a high removal percentage, carbon has the advantage that it can be used to treat many hazardous substances. Therefore, stockpiling large quantities of activated carbon for spill treatment would not be unreasonable. The water-permeable bag approach would have a number of advantages, but it must be shown that appropriate interaction can be obtained between the pollutant and the carbon.

Treatment by Neutralization

Neutralization is being investigated as a potential treatment for spills of chlorine. When ammonia (NH_3) is spilled in water, it will hydrolyze to ammonium hydroxide (NH_4OH), a weak base. Ammonium hydroxide neutralization experiments were conducted on a laboratory scale considering the following treatments:

1. Neutralization with carbon dioxide gas, which hydrolyzes to carbonic acid (H_2CO_3) in water;
2. Neutralization with acetic acid (CH_3COOH), a weak acid;
3. Neutralization with a dilute solution (10%) of hydrochloric acid, a strong acid.

For the carbon dioxide tests, the gas was bubbled into a beaker by means of a diffuser. The pH of the ammonium hydroxide solution was monitored throughout the experiment. In one test, the initial concentration of ammonium hydroxide was 1,000 ppm. Gas flow rates of 1 cu ft/hr and 2 cu ft/hr were used. The pH as a function of time for 500 ml of test solution is shown in Figure 7. The figure shows that neutralization occurs reasonably rapidly, and that there is sufficient buffering to preclude overdoses sufficient to produce highly acidic residual reactions.

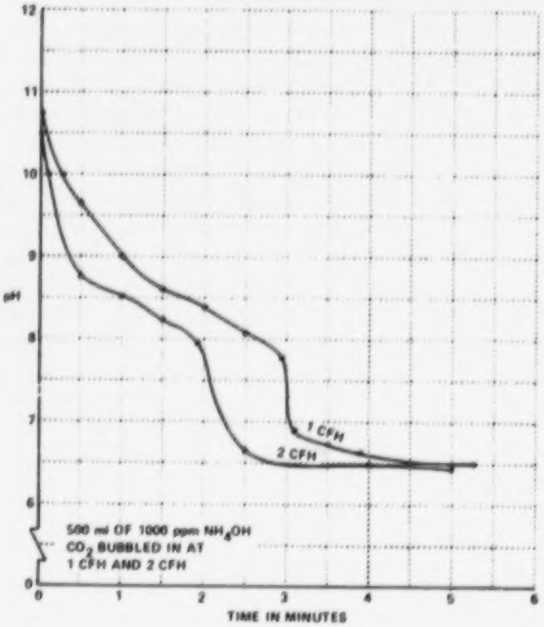

Figure 7: Neutralization of 1000 ppm Ammonium Hydroxide with Carbon Dioxide

For the experiments with acetic acid, an initial sodium hydroxide solution of 10,000 ppm concentration was treated with 10% acetic acid. Figure 8 shows the pH as a function of the amount of acetic acid added to the test solution. The figure shows that pH will drop rapidly from 7 to about 5.5 if overdosed, but danger of further pH reduction is lessened by buffering at pH 5.0. The reaction products are NH_4^+, $C_2H_3O_2^-$, and H_2O.

The neutralization of a 10,000 ppm ammonium hydroxide solution with 10% hydrochloric acid is

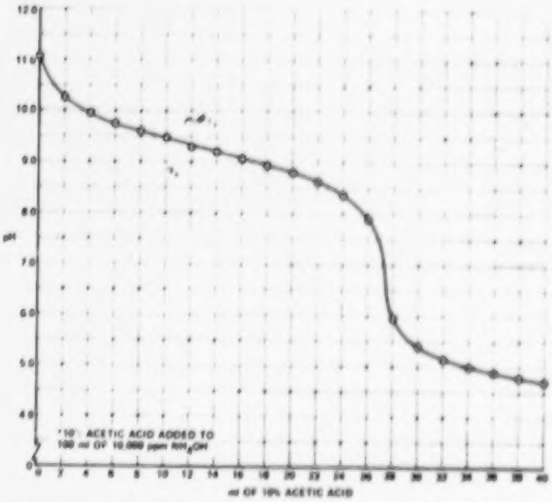

Figure 8: Neutralization of 10,000 ppm Ammonium Hydroxide with 10% Acetic Acid

shown in Figure 9. When a critical amount of HCl is added, the pH drops rapidly from about 7 to about 2, thus presenting a severe danger of overdose to highly acidic levels.

It appears that neutraliz[illegible]n with carbon dioxide or acetic acid (vinegar) [illegible] prefereable. For using CO_2, effective means for diffusing the gas in the water must be found to prevent loss of large quantities of the gas to the atmosphere. Bioassays are being performed to determine which of these treatment materials is least detrimental to test organisms.

The solubility of chlorine in water is about 0.7 grams/100 ml at 70°F. About 50% of the chlorine in a saturated solution remains as molecular chlorine, and the remaining 50% reacts with water to give about 25% HOCl and 25% HCl according to the following reaction:

$$H_2O + Cl_2 \longrightarrow HOCl + HCl$$

In the presence of activated carbon which acts in this case as a catalyst, the above reaction proceeds much more rapidly and completely to the formation of HCl. Laboratory experiments were conducted to determine carbon dosages required to convert molecular chlorine (and HOCl) to HCl and the amount of sodium carbonate (a basic salt) required to neutralize the resultant acid solution. The results of experiments conducted with Aqua Nuchar A at an initial chlorine (Cl_2) concentration of 1,460 ppm are presented in Table IX. The data show that activated carbon is very effective in reducing molecular chlorine concentration. Thus, for example, a carbon dosage of 5,000 ppm reduces initial chlorine concentration of 1,460 ppm to 40 ppm, a 95% reduction. As a result of the catalytic action of activated carbon on molecular chlorine, chloride ion concentration increased and pH dropped. The amount of Na_2CO_3 necessary to adjust pH's of treatments to neutrality was determined titrimetrically, and the data are shown in columns 5 and 6 of Table IX. Sodium carbonate was chosen for acid neutralization because it acts as a weak base upon hydrolysis and overdosage is less likely to occur.

Heavy Metal Precipitation

For spills of various heavy metal compounds, treatment can be effected through the addition of sodium sulfide to form the heavy metal sulfide precipitate. This form of treatment removes the active heavy metal ion from solution and converts the metal to a form which is relatively harmless. The investigations of heavy metal precipitation have been carried out in laboratory bench experiments, in a flow channel ten centimeters wide and 38 feet long, and in a creek located in Western New York State.

In the flow channel experiments, stoichiometric quantities of sodium sulfide were added to the flow channel in solution form to treat known quantities of various heavy metal compounds, also introduced into the channel as solutions. Different treatment procedures were studied, including simultaneous dumping of the metal and sodium sulfide solutions at the same point in the channel, and dumping of the two solutions sequentially at different points in the channel. In the flow channel tests, specific ion electrodes were used to monitor sulfide ion concentration and divalent cation concentration at various positions in the channel. The tests showed that mixing of the sulfide treatment and the metal

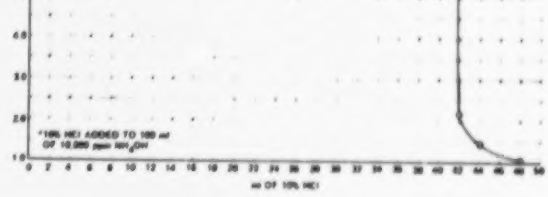

Figure 9: Neutralization of 10,000 ppm Ammonium Hydroxide with 10% Hcl

TABLE 9

Adsorption of Chlorine* on Activated Carbon

Carbon Dosage (ppm)	Residual Chlorine (Cl_2) Concentration (ppm) (1)	% Reduction Chlorine (Cl_2) Concentration (2)	Residual Chloride Concentration (ppm) (3)	Final pH (4)	Quantity of Na_2CO_3** to neutralize acidity (pH = 7.0) (mg/liter) (5)	Na_2CO_3 to Chlorine Ratio for neutralization (6)
0	1,460	0	875	1.47		
100	590	59	600	1.49	1,765	1.20
500	380	73	600	1.38	2,000	1.37
1,000	230	84	700	1.24	2,940	2.02
5,000	40	97	1,400	0.97	4,350	2.98
10,000	10	99	1,400	0.97	4,530	3.10
50,000	5	99	1,300	1.00	4,530 (estimated)	3.10

*Initial Cl_2 concentration = 1,460 ppm
Carbon = Aqua Nuchar A
Carbon time = 1 hr
**Concentration of Na_2CO_3 titrant = 100 g/l

spill occurred rapidly and nearly completely for both treatment procedures as evidenced by the fact that no detectable ferrous ions were present downstream of the treatment point, and the residual sulfide concentration downstream reached a peak of only 10^{-6} molar. In one test in which 520 mg of iron were spilled in the test channel, analysis of a sample of water taken at the channel outlet and a determination of the stream volume through which the spill had spread indicated that, at most, only 7 mg of the original 520 mg of iron remained in solution. The flow channel tests showed further the importance of turbulence on the settling rate of the precipitates. At flow rates of a fraction of a centimeter per second, a spill of ferrous sulfate and subsequent treatment with sodium sulfide resulted in a thin layer of ferrous sulfide deposited over the entire length of the channel from treatment site to outlet with considerable quantities of ferrous sulfide flowing out of the channel. At higher flow rates, very little ferrous sulfide remained in the channel.

Following the initial flow channel tests, a field experiment was performed in a creek in Western New York State. In the vicinity of the spill, the width of the creek varies from about six meters to eleven meters, and the depth reaches a maximum of 40 centimeters per second. For this first field test, spills of 0.5 mole of ferrous ion (from ferrous sulfate) and 0.5 mole of sulfide (from sodium sulfide) were introduced simultaneously into the stream within a few centimeters of each other. A ferrous sulfide precipitate formed rapidly and could be followed downstream for 40 meters to the vicinity of a bridge where the creek deepens and the current is correspondingly reduced. Most of the particles settled in this region within five to seven minutes following the spill. Only a very faint cloud of very small particles was noted downstream. The average stream velocity upstream of the bridge was 18 cm/sec, while the velocity immediately downstream of the bridge was 7 cm/sec. Analysis of 19 samples taken at various locations indicated that the concentration of ferrous ion in the center of the spill was small (less than 7.5 ppm) compared to the concentration of precipitated iron, which varied from 140 ppm to 0 ppm. Bottom samples showed appreciable concentrations of insoluble iron compounds both above and below the spill site. No adverse effects on fish life in the area were observed.

Following this first preliminary field test, a more elaborate field test was conducted some weeks later at the same test site. In the second test, a larger number of samples, both physical and biological, were obtained, and a conductivity probe and specific ion electrodes were used for monitoring conditions in the stream. In this second field test, the treatment was applied downstream of the spill location. The spill consisted of 5 moles of ferrous sulfate in 0.5 molar solution. The spill was treated ten meters downstream of the spill point with 5 moles of sodium sulfide poured into the stream in several slugs spaced along the length of the ferrous sulfate plume. The spill was detected at the treatment site by using a thin stream of sodium sulfide solution to mark the leading edge of the spill with a black ferrous sulfide precipitate. The spill was also detected by the conductivity sensor in the stream just above the treatment point. Values of sulfide ion concentrations and pH were measured as the spill passed points 13, 27, 57, and 85 meters downstream of the treatment point. No effect of the spill and treatment on the pH of the stream was detected. Sulfide ion measurements at the four monitoring sites are shown in Figure 10. The four separate curves, labeled mm 13, mm 27, mm 57, and mm 85, show the sulfide ion concentration (molar) at points 13, 27, 57, and 85 meters downstream of the spill point as a function of time. The peak sulfide ion concentration measured at meter mark 13 was only 2 x 10^{-5} molar; and at meter mark 27, the peak had decreased by more than an order of magnitude. The sulfide ion concentration at sites farther downstream were insignificant.

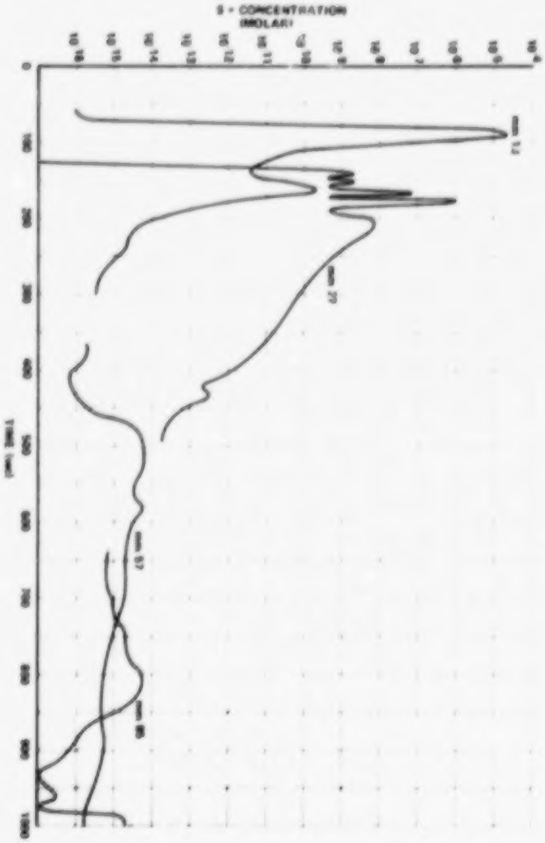

Figure 10: Sulfide Ion Concentration vs Time at Several Sampling Points

Creek water samples were collected for laboratory analysis at points 17, 30, 43, 60, and 80 meters downstream from the treatment point and at a number of points farther downstream. These samples were analyzed for dissolved and precipitated iron. The peak concentration of dissolved iron in any sample was 0.6 ppm, while iron in the form of ferrous sulfide was found in concentrations as high as 26 ppm. The data illustrated a rapid spreading of the precipitate in the stream. A major mechanism of the spreading was the transfer of the precipitate between eddies and slow flowing parts of the stream, and the main current. After passage of the main body of the spill, these relatively stagnant areas were observed to remain black with suspended precipitate which gradually fed back into the main channel. The black cloud of precipitate was discernible several hundred meters downstream of the spill site, indicating that settling was far from complete in this length. White sheets placed on the stream bottom in likely settling spots failed to accumulate significant deposits of the sulfide.

A comparison of observations made for the first field test and the second field test shows that settling occurred much more rapidly in the first test. A possible explanation is that in the second test the spill and treatment were not introduced simultaneously into the stream at the same point. The significance of this point is that when sodium sulfide treatment is applied at high concentrations of ferrous sulfate, larger particles are formed than when the treatment is applied under dilute conditions. It is likely that in the second test, where treatment was applied downstream of the spill, smaller particles were formed than in the first test, because the spill was allowed to dilute before treatment. Further tests are planned to determine what factors affect settling rate of sulfide precipitates.

Biological studies performed before and after the second spill suggest that the spill did not harm aquatic life at the site. Approximately 75 minnows (*Notropus* sp.), exposed to the black plume of ferrous sulfide were caught and returned to the laboratory alive. The fish were placed in an aquarium and observed continuously over a period of several weeks. No signs of any harmful effects were observed. Benthic studies at three sites along the spill site, both before and after the spill, yielded approximately the same percentages of organisms per comparative sample.

Bioassay studies on fish and algae are being conducted to determine the effects of the sulfide precipitate, as well as of the sulfide treatment itself in the event of an overtreatment with sodium sulfide. If it is determined that the precipitate can cause harmful effects on aquatic life, then removal will be imperative. Preliminary experiments were performed in the six centimeter diameter flotation column to evaluate the feasibility of removing ferrous sulfide precipitate by air flotation. Cetyldimethylbenzylammonium chloride was used as the collector, and the pH at the start of flotation experiments was 6.8. Ferrous sulfate was mixed with the stoichiometrically correct amount of sodium sulfide to produce the ferrous sulfide to be removed. Under optimum conditions, 84% of the ferrous sulfide was removed in foam comprising 17% of the original solution.

Treatment of Land Spills

For spills of hazardous materials on land, rapid response methods must be available to prevent the spilled material from reaching watercourses. Two candidate methods for treating land spills currently under investigation are: (1) treatment of the ground surface to prevent percolation of the pollutant; and (2) treatment to promote polymerization, congealing, or gelling of the spilled material to prevent spreading.

In tests using methanol, phenol solution, and acrylonitrile, two types of soil (clay and sand) were treated with several different materials to determine their effectiveness for sealing the soil surface. In these tests, the soils were first coated with the test treatment material and then the pollutant solutions were poured over them. Observations were then made of the ability of the treated soil to withstand penetration of the pollutant. In preliminary experiments, a fluorinated polymer proved to be the best of several materials tested. Even relatively thin coatings obtained by spraying the treatment material on the soil were effective in preventing penetration of the test pollutants.

For the gelling experiment, a sample of a nontoxic, protein-based, water-gelling material normally used in fighting forest fires was obtained. When a small quantity of this material (~0.2-0.4% by weight) is added to the water, a thick, viscous gel is formed. It was found that water treated with this dry powder "sets up" in less than three minutes, and that the viscosity of the resultant gel is easily adjusted by the amount of gelling agent used. In a series of jar tests, a mixture of gelled water and acrylonitrile was found to form a two-phase system with the less dense acrylonitrile forming a separate layer on top of the gelled water. Mixtures of gelled water and methanol were found to form homogeneous gelled masses if mixed well. Mixtures of phenol and gelled water were found to form two-phase systems with the denser, ungelled phenol on the bottom and gelled water on top.

Additional tests to determine the effectiveness of a water gel as a treatment method for land spills were conducted using columns containing sand and a loamy-textured field topsoil. Two conditions were evaluated, the first involving the addition of a toxic liquid to the sand or soil column followed immediately by addition of gelled water. For the second test condition, a layer of gelled water was poured over the soil and then the pollutant was added.

For the first test condition, it was found that the addition of gelled water to loamy soil or sand following addition of acrylonitrile was effective in preventing ground infiltration. In this case, the lighter-than-water, and relatively insoluble, acrylonitrile was displaced by the heavier gelled water and actually floated to the top. The gelled water penetrated very slowly and thus effectively prevented movement of acrylonitrile into the soil or sand. The addition of gelled water to either spilled methanol or phenol had little efficacy in retarding soil or sand penetration.

Under the second test condition, acrylonitrile did not infiltrate a sand or loamy soil column covered previously with ~0.5 inch of gelled water. In the case of methanol, it was found that the effectiveness of gelled water in retarding infiltration depends on the thickness of the gelled water layer. A 5/8 inch thick layer of gelled water over a loamy soil retarded penetration of a one-inch layer of methanol for 48 minutes. However, increasing the thickness of the gelled water layer to 1-3/4 inches delayed penetration of the methanol to three hours. In tests with phenol, the phenol quickly displaced even a two-inch thick layer of gelled water and infiltrated into the soil. Additional experiments indicated that infiltration of benzene could be effectively retarded, whereas infiltration of carbon tetrachloride could not.

From the observed behavior of the first substances discussed above in the presence of gelled water, predictions regarding other hazardous substances can be made. Density and water solubility appear to be very important. Thus, it appears that substances that are less dense than water and either insoluble or only slightly soluble may be prevented from infiltrating soil by treatment with gelled water. Ground infiltration of substances which are miscible in water may be retarded by prior treatment of soil surfaces with thick layers of gelled water. Percolation of substances which are heavier than water and insoluble, or only partly soluble in water, will not be retarded by gelled water. The application of gelling agents has a potential twofold advantage. First, once gelled, the materials cannot penetrate the soil. Second, they are immobilized to prevent further spreading and subsequent transport into watercourses.

In the course of investigating means of congealing land spills, a number of different possible treatment agents were investigated. One of the most effective materials found for congealing acylonitrile, acetone cyanohydrin, and phenol was an acrylic latex emulsion. For a 2:1 mixture of acrylonitrile and emulsion, instant thickening occurred, and the mixture coagulated completely upon mixing. Experiments are currently underway on the polymerization of "monomer" chemical spills as a means for immobilizing them. Some success has been achieved to date, but in general, it is difficult to obtain rapid polymerization under the ambient conditions that would be typical of real spill situations.

CONCLUSIONS

At this time, investigations are still in progress for all treatment methods discussed in this paper. Therefore, it is premature to state definite conclusions concerning the effectiveness of these methods for real spill situations. The following conclusions are presented with the realization that subsequent investigations made in the course of this program may require that they be modified.

It appears that air flotation for retrieving activated carbon following spill treatment is not practical because of logistical considerations. Effective treatment of water spills by the addition of activated carbon is potentially promising, but either effective means must be available for removing the carbon after treatment or it must be shown that allowing the pollutant-laden carbon to remain in the water will not have an adverse effect on the environment. For precipitation of heavy metals as a treatment technique, similar conclusions are drawn concerning air flotation for retrieving the precipitate. The neutralization of ammonia spills by the addition of carbon dioxide gas or acetic acid appears to provide a practical treatment method; however, bioassay tests to determine the potential effects on the environment have not been completed at this time. It appears that land spills of a number of hazardous materials can be controlled by treating the soil surface and/or congealing or gelling the spilled material.

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Many people at CAL have been deeply involved in, and have made significant contributions to, the work reported in this paper and have been responsible for suggesting the treatment methods discussed. In a sense, they should be considered as co-authors. Richard P. Leonard, John G. Michalovic, and Lawrence K. Wang are responsible for the experiments pertaining to activated carbon treatment and land spill control by soil treatment and gelling. Dr. Murray P. Strier has led the investigations of land spill control by congealing and polymerization. Edward W. Hodgson, Jr. and Ditmar H. Bock are responsible for the investigations of precipitation as a means for treating water spills of heavy metals. Mrs. Sharron Pek performed the biological studies in support of the field tests. The many helpful suggestions and recommendations of Douglas B. Dahm, Head of the Environmental Systems Department, Dr. Robert E. Baier, Head of the Chemical Sciences Section, and Clayton J. Schneider, Jr. are deeply appreciated.

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THE APPLICATION OF SORPTION PROCESS FOR IN SITU TREATMENT OF HAZARDOUS MATERIAL SPILLS*

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INTRODUCTION

Sorption processes are highly effective for removing many different substances from water, and application of sorption techniques has been identified as one of the most potentially promising approaches to *in situ* treatment of hazardous material spills.[1] The principal advantages of using sorption processes for this purpose are: (1) Treatment can be accomplished without the addition of chemical reagents to the water; (2) one sorbent can be used to remove a large number of different substances from water; and (3) the sorbent collects and holds a hazardous material in a relatively innocuous form for long periods of time. The term "sorption" as used in this paper applies to both physical sorption (e.g., surface attraction as in activated carbon) and ion exchange, although the latter may be interpreted differently as a matter of personal preference.

Sorption may be accomplished either by batch treatment or by column treatment. Batch treatment is carried out by mixing the sorbent with the solution to be treated for a specified period of time, after which the sorbent is separated from the solution for disposal or regeneration and reuse. This method is simple and may be carried out with relatively low-cost equipment. Column treatment is accomplished by percolating the solution through a bed of the sorbent until some level of the sorption capacity is utilized. The sorbent in the column is usually regenerated at this point and the loading cycle repeated. Column treatment is generally more efficient than batch treatment, and lower effluent concentration values may be attained. The major disadvantage of column treatment with respect to field use in treating spills of hazardous materials in water is the relatively long time period required to set up and operate the equipment needed. Because response and treatment time must be rapid to minimize dispersal of the hazardous material from the site of the spill, batch treatment appears most feasible for field use.

Recovery of the sorbent after treatment is necessary to avoid problems related to slow desorption of highly toxic material and for aesthetic reasons. Most sorbents will sink when applied to water, which complicates retrieval of the sorbent. The use of floating sorbents, however, would facilitate recovery, because oil skimming or similar equipment may be used to retrieve the sorbent following *in situ* use. This paper deals with the development and evaluation of floating sorbents for use in treatment of hazardous materials spills in water.

DISCUSSION

Floating Ion Exchange Resins

Ion exchange resins are effective for removing and/or neutralizing a broad spectrum of hazardous ionic substances from water. These substances include acids, bases, and toxic salts where either the cation or the anion or both are toxic to some degree.

The use of ion exchangers for treating spills of hazardous materials involves replacement of the hazardous material with a less nocuous material. For acids and bases the H^+ and OH^- ions are neutralized to water, and the anion or cation corresponding to the acid or base is sorbed by the exchanger. There-

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fore, the acid or base is essentially removed from the water, and a corresponding amount of salt does not remain as would be the case if the acid or base were chemically neutralized. The treatment of a salt spill (e.g., $CuSO_4$) would most probably involve the replacement of one of the ions (e.g., Cu^{+2}) with a less objectionable ion (e.g., Na^+).

The degree of sorption for a particular ion under equilibrium conditions is largely a function of: (1) the concentration of that ion; (2) the concentration and types of competing ions; and (3) temperature. A number of different types of ion exchange resins are available under the categories of cation exchangers or anion exchangers. The cation exchangers can be divided into different types depending on the acid strength of the groups. Strong acid groups such as $-SO_3^-$ remain ionized even at low pH and can function in acid solutions. In contrast, weak acid grous such as $-COO^-$ are ionized only at high pH. At low pH they combine with H^+ to form undissociated -COOH and no longer act as fixed charges where an exchange of ions can take place. For example, a weakly acidic cation exchange resin would not be effective for removing ammonium ion from a solution at pH3 because of the resin's strong affinity for hydrogen ion. Under neutral to basic conditions, as in the case of an ammonia spill, a weakly acidic cation exchange resin could be effective for both neutralizing the basicity and sorbing the ammonia. The titration curve of a weakly acidic resin is illustrated in Figure 1 along with that of a strongly acidic resin. The advantage of using a weakly acidic ion exchanger for treating a caustic spill is that an overdose would not cause an overreaction which would produce acid instead of neutral conditions. Anion exchangers which vary in base strength and act in a manner similar to cation exchangers are also available.

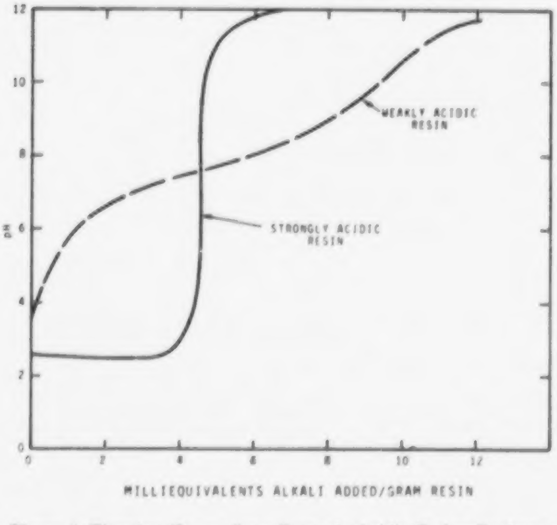

Figure 1: Titration Curves for a Strongly Acidic Cation Exchange Resin and a Weakly Acidic Cation Exchange Resin.

Titration in 0.01 M KCl (5)

It is anticipated that floating sorbents will be used *in situ* by injection at the bottom of a watercourse and allowed to float to the surface through the zone of contamination. A major concern with a floating sorbent relates to the kinetics of removing various hazardous polluting substances as the sorbent moves from the bottom of a watercourse to the surface of the water. In the case of columns, kinetic problems are solved by adjustment of the throughput rate to achieve the necessary residence time to effect the desired degree of removal. But kinetic problems are not so simply solved in a buoyant sorbent system. The sorbent must perform its function with only one pass to the surface.

The controlling parameters involved in a free-water mass-transfer system include: temperature, concentration of solute, particle velocity, and particle surface area. Obviously, the first two parameters are functions of the location and nature of the spill and cannot be practically controlled in a free water environment. (Indeed, the purpose of applying a countermeasure is to reduce the concentration of the solute [hazardous polluting substance] to some acceptable level). However, particle velocity and particle surface area can be controlled through adjustment of the particle size.

Since mass transfer rates are proportional to surface area, the division of a large particle into several smaller ones increases the surface area and thus accelerates the mass transfer rates. Reduction in particle size also reduces the rate of rise of a floatable media, since buoyancy is a function of r^3 while drag is a function of r^2. Reduction of the rate of rise increases the residence time as the media rises to the surface. Thus, reduction of particle radius causes an increase in the rate of mass transfer to occur. Adjustment of media density can also be utilized to increase the contact time.

Boyd, *et al*[2] note that for organic zeolites in the 60 to 70 mesh range, up to 90 percent of the theoretical capacity can be achieved within 30 seconds. Kressman and Kitchener[3] found phenosulphonic resins reach 90 percent of capacity in 2 to 9 minutes with simple cations. Helfferich[4] makes similar observations for strong acid and base exchanges. It should be possible to adjust the rise rate of the selected media to provide the several minutes required for utilizing the major portion of the media's capacity.

Two types of resin were selected for study in preparation and evaluation of floating ion exchangers. These were: (1) a weakly acidic carboylic resin prepared from acrylic acid and a suitable crosslinking agent and (2) an intermediate epoxypolyamine resin prepared from epichlorohydrin and polyethyleneimine. The exchange resins were rendered buoyant by incorporating hollow glass microspheres* in the resin granules or beads. A bulk polymerization technique was employed to produce the floating acrylic cation exchange resin whereas a suspension polymerization technique was employed to prepare the floating epoxypolyamine anion exchange resin. The latter produces spherical beads suspended in hot mineral oil during the polymerization step.

The ultimate exchange capacity of a floating acrylic cation exchange resin, prepared from acrylic acid and ethylene glycol dimethacrylate, was found to be 8 milliequivalents per gram of dry resin (includes weight of hollow glass microspheres). The titration curve for the resin is given in Figure 2. Two different mesh sizes of this resin in the H+ form were floated through a 5 ft. column of water (2 in. diameter) containing 200 mg/l or NaOH. The application consisted of 2000 mg/l of 25 x 70 mesh resin and the same quantity of 20 x 50 mesh resin both released dry from a bottle at the bottom of the column. The finer 25 x 70 mesh resin removed 82 percent of the alkali compared to 66 percent removal by the coarser 20 x 50 mesh resin. The time for the bulk of the resin to float to the surface was approximately ten minutes for both mesh sizes.

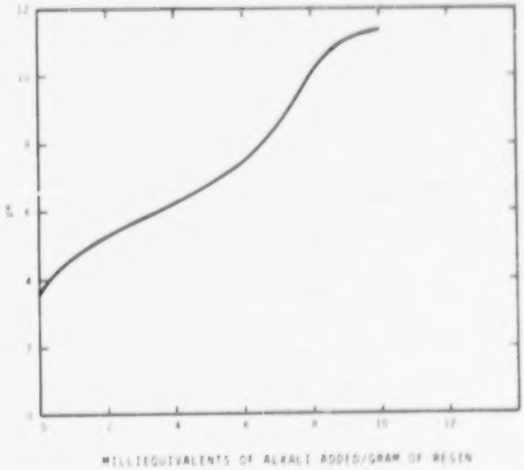

Figure 2: Titration Curve for Floating Acrylic Ion Exchange Resin

Titration in 0.2 M NaCl

Another floating acrylic cation exchange resin was prepared using acrylic acid crosslinked with divinyl benzene with hollow glass microspheres incorporated in the resin granules. An alkali removal of 89 percent was obtained with a 30 x 70 mesh size with this resin.

A floating anion exchange resin was prepared by suspension polymerization in mineral oil using epichlorohydrin and tetraethylene pentamine in a 3:1 mole ratio plus hollow glass microspheres. This resin was found to have an ion exchange capacity of 4 milliequivalents per gram of resin. A titration curve for the resin is given in Figure 3. The resin beads used for evaluation were largely in the 30 to 50 mesh size with 12 percent + 30 mesh and 9 percent - 50 mesh. When released to float up through a 5 ft. column of water, containing 183 mg/l HCl, the resin removed 61 percent of the acid at an application ratio of 2000 mg of resin per liter of water. This removal is somewhat less than the removal of NaOH by floating acrylic cation exchange resin under comparable conditions which is believed due to the smaller ion exchange capacity of the epoxypolyamine resin (4 meq/g vs. 8 meq/g). In both cases, however, only a small fraction of the available ion exchange capacity was utilized. A smaller mesh size is considered to be more important in increasing the removal than adjusting the resin bead density to a level just under that of water. Resin bead density cannot be adjusted too near to that of water since the density of the bead will increase as it sorbs ions from the water to replace either H+ of OH- ions. The resin bead will rise more rapidly at first when its density is the least.

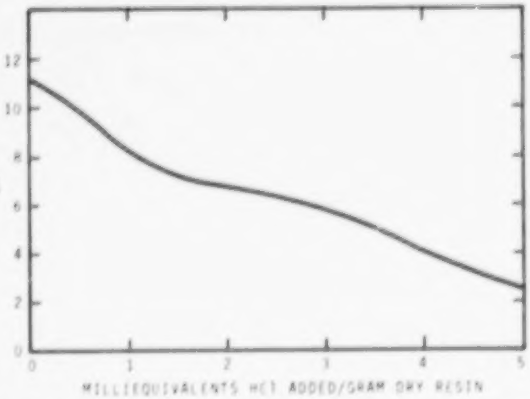

Figure 3: Titration Curve for Floating Epoxypolyamine Anion Exchange Resin

Titration in 0.2 M NaCl

Floating Physical Sorbents

Physical sorption results from the attractive forces that are present at the interface of two phases. The surface of a solid will attract and hold molecules present in either gases or liquids. The amount held per unit area of the surface is relatively small, but the amount becomes a significant fraction of the total mass of the solid phase when the surface area per unit of mass becomes very large. The surface area of a good activated carbon for example, will be on the order of 1000 square meters or more per gram of carbon.

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*Eccosphere(R) manufactured by Emerson and Cuming Inc., Canton, Mass.

A number of physical sorbents are available for removing non-polar materials such as organic substances from water, but the best known and most widely used physical sorbent is activated carbon. An investigation of available active carbons with the desired floatability disclosed two commercial granular carbons which resist wetting and will remain floating for long periods of time. These are Nuchar C-190 (R) and Nuchar WA(R) + 30 mesh. Various mesh sizes of these carbons both wet and dry were evaluated for their uptake of phenol by floating the carbons through a 5 ft. column of phenol solution (185 mg/l) buffered at pH 6.5. The carbon was released from a bottle at the bottom of the column at an application ratio of 2000 mg carbon per liter of solution. The results of these experiments are illustrated in Figure 4. The dry carbon was prepared by oven drying at 110°C for 16 hours and the wet carbon was contacted with water for 2 hours and then filtered to remove interstitial water before use. The time required to float the bulk of the carbon through the 5 ft. column varied from 3 and 12 minutes for the dry and wet 30 x 50 mesh carbon, respectively to 20 and 25 minutes for the dry and wet 200 x 325 mesh carbon, respectively. Nuchar C-190 was selected for further study on the basis of its superior sorbtive ability and floatability. In addition, the Nuchar C-190 was found to contain a smaller percentage of sinking granules than the Nuchar WA. A mesh size of 100 x 325 was selected for application.

Larger scale experiments were conducted in a 6 in. diameter, 6 ft. deep column of tap water containing 200 mg/l of: (1) phenol, (2) oil emulsion of Malathion*, and (3) an oil emulsion of Diazion(R). Removals of 86 percent, 82 percent, and 86 percent, respectively, were obtained by floating 1000 mg/l of 100 x 325 mesh carbon through the water. The concentration of phenol and pesticide did not vary significantly at various depths through the column after floatation of the carbon. Carbon containing sorbed phenol was observed to remain floating for at least two days following application. The carbon was found to be effective for removing phenol in the 0°C to 25°C temperature range.

Delivery Systems

Mechanical subsurface injection by means of slurry pumps installed on ships is probably the most desirable method of delivery in areas such as ports and harbors where such equipment is readily available. However, in remote areas, rapid transport of subsurface injection equipment may not be feasible. Therefore, techniques are under development which lend themselves to air transport and injection of the floating solvents.

Systems currently under active consideration for delivering the floating sorbent to the bottom of body of water where a spill of hazardous material has occurred include the following:

1) Ice cakes containing floating sorbent and sufficient ballast such as sand or gravel to sink the ice cake.
2) Unfired clay-sand containers which disintegrate under water to release the floating sorbent.
3) Plastic bottles which separate from the ballast and float to the surface for recovery following release of the sorbent. Water soluble seals could be employed to contain the sorbent and ballast during delivery.

These systems were selected to avoid littering the area concerned with empty containers or polluting the water with foreign matter such as gelatine (capsules) and cardboard. The use of ice cakes represents the most efficient system from the viewpoint of the least amount of ballast required. In addition, the sand or gravel ballast is the least objectionable material that can be deposited in most cases. The major disadvantage of the ice is the refrigeration requirement during storage. Preliminary results with unfired clay-sand containers are promising and this system also involves natural materials for ballast. Plastic bottles attached to concrete ballast with water soluble material have been successfully tested in the laboratory. All systems are undergoing further investigation to assure that the containers can withstand an air drop since air transport is considered to be the most probable means of delivery in remote areas.

It is to be noted that a considerable amount of ballast is required to sink the floating sorbents. Dry Nuchar C-190, for example, has a bulk density of 7-10 lbs. per cu. ft. Therefore, approximately 100 lbs. of concrete ballast (SpGr = 2.3) will be required to sink a cubic foot of dry Nuchar C-190. Wetting

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(R)Products of Westvaco, Covington, Virginia.

*Malathion is the trade name for the insecticide 0,0-dimethyl dithiophosphate of diethyl mercaptosuccinate.

(R)Diazinon is the registered trademark for the insecticide 0,0 diethyl 0-(2-isonropyl-4-methyl-6-pyrimidinyl) phosphorothioate manufactured by the Geigy Chemical Company, McIntosh, Alabama.

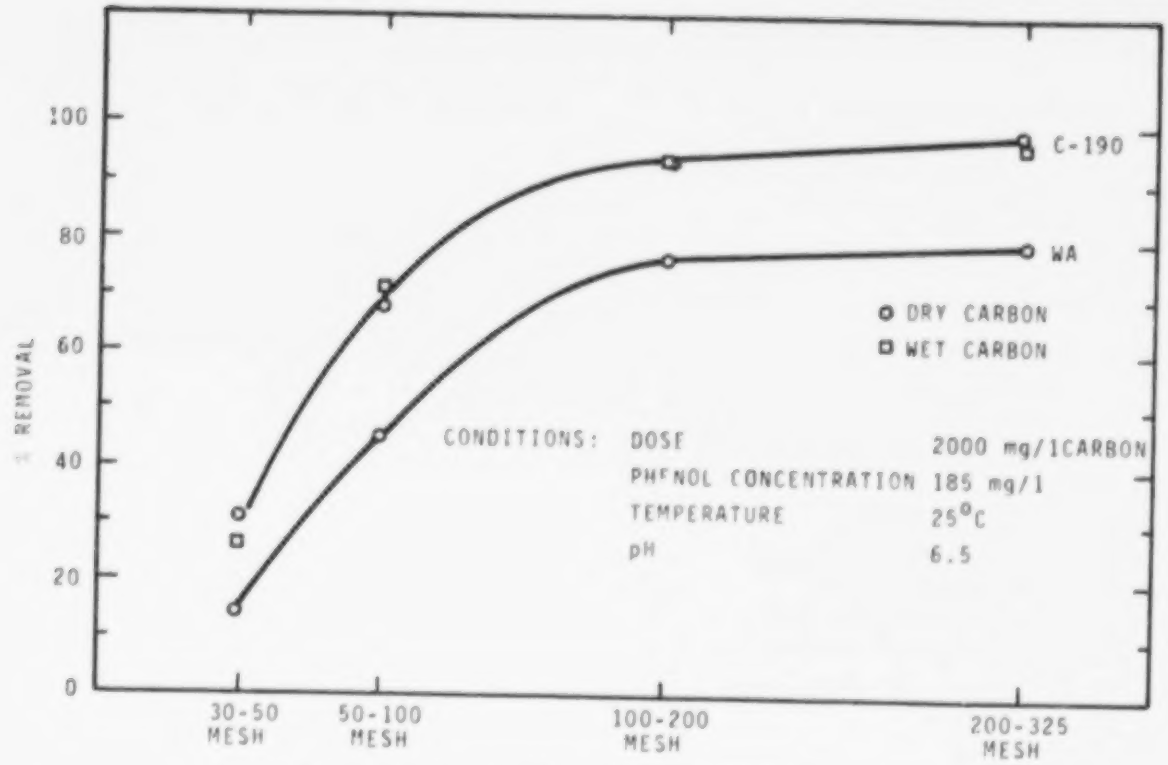

Figure 4: Comparison of C-190 with WA for Removal of Phenol

carbon to fill the interstices with water reduces the amount of ballast required but eliminates the use of soluble seals for releasing the carbon under water from bottles and also the use of unfired clay-sand containers. The use of ice, whereby water fills the interstices, circumvents this problem to a large degree.

SUMMARY AND CONCLUSIONS

The results of laboratory studies show that floating sorbents are highly effective for removing hazardous materials from water when applied as small particles beneath the surface. The sorbents remove the hazardous materials while rising through the contaminated water. A light weight commercial activated carbon was found to be particularly effective for removing organic substances from water. The active carbon can be pulverized to a small mesh size (100 x 325) which floats slowly to the surface of water. The small mesh size both enhances the speed of sorption and increases the contact time with the water by flow floatation.

Floating ion exchange resins were prepared which are effective for removing acid or alkali from water. Hollow glass microspheres are incorporated in the resin granules for buoyancy. Due to the use of larger particle sizes (minimum 70 mesh), only a fraction of the resin's total exchange capacity is utilized in floating to the surface.

Delivery systems are being investigated which employ air drops of the floating sorbents into the water where the spill occurred. This method allows the shortest response time to a reported spill. Delivery packages under study for the floating sorbents include: (1) ice cakes containing the floating sorbent and ballast, (2) unfired clay-sand containers, and (3) recoverable plastic containers. Field demonstrations are planned on the use of floating sorbents for removing 10 to 500 lbs. of hazardous materials spilled in water contained in large concrete lined basins.

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THE RESPONSE OF AQUATIC COMMUNITIES TO SPILLS OF HAZARDOUS MATERIALS

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Aquatic ecosystems have the ability to assimilate a certain amount of waste material and maintain near normal function. With the constant use and reuse of water by industries, agriculture and municipalities, the function may be altered or disrupted if the assimilative capacity is exceeded. The ability of a river or lake to assimilate wastes is governed by the capacity of the system to transform them before they reach deleterious levels. If an overload occurs due to a spill of a hazardous material, the system is disrupted and the transforming capacity may be substantially reduced.

The capacity of a system to receive and assimilate spills of hazardous materials without environmental damage is determined by the physical, chemical and biological conditions of the receiving system. Introduced materials may be transported, rendered, converted respired, incorporated, excreted, deposited and thus assimilated by the system. However, not all systems can receive and assimilate the same quantity or kinds of waste material and, even within a single system, this capacity will vary. The capacity of each system to resist shock loadings of wastes without significant damage is a function of complex environmental factors. Physical factors in a river or stream such as flow velocity, volume of water, bottom contour, rate of water exchange, currents, depth, light penetration, temperature, etc., as well as the biological factors, govern in part the ability of a system to receive and assimilate waste or spills of hazardous materials.

The unique chemical characteristics of different systems govern in part the kinds and quantity of wastes a system can receive without damage. Due to synergistic or antagonistic interactions with receiving chemical water quality, the effects of a potentially hazardous material on a wide variety of receiving systems is difficult to predict.[1] The modification of the toxicity of potentially hazardous materials by chemical characteristics such as, hardness, alkalinity, pH, buffering capacity and nutrients may markedly affect the ecological effects.

The biological community present in a receiving system is determined partly by the physical and chemical characteristics of the system and partly by the kinds of organisms that colonize the area (this latter is often a matter of random chance). Obviously, if systems vary chemically and physically, they then vary in the components of the biological community present. Thus the effects of a potentially hazardous material introduced through a spill may vary from one system to another, because not all organisms will respond in the same way to a particular concentration of a hazardous material. However, in the past twenty years a great deal of evidence has accumulated which indicates that biological communities are not a haphazard collection of species, thrown together by the whims of nature, but rather that they have a fairly well defined structure. While the individual components of the aquatic community may vary from one aquatic system to another, the structure of the communities are remarkably similar in most temperate zone fresh-water systems in industrialized areas.

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[1] There are some well regarded water pollution specialists in Great Britain who believe this is possible, and they have evidence supporting their point of view (Herbert and Van Dyke, 1964; Jordan and Lloyd, 1964; Brown *et al.* 1965).

Essentially this structure is due to the fact that energy flows through a diverse network of species called a food web (Figure 1). Although the number of individuals at any one energy level may vary, the number of species involved in the web (or to put it another way, the number of qualitative differences possible in the system), remains relatively constant under natural conditions. The number of components of species in this energy system also remains remarkably constant from one river basin to the next, and at various points within a basin as well, despite the fact that the types of species which comprise the system may differ at various sampling points. This is merely a restatement of the survival of the fittest principle with the corollary assumption that there are several species available to do each particular job, and that one of these may outcompete its rivals in one river system, but not in all river systems. Recognition of this principle obviates the need for a detailed study of a miscellaneous collection of aquatic organisms in each receiving stream, and restricts the problem to the study of basic changes in the system itself.

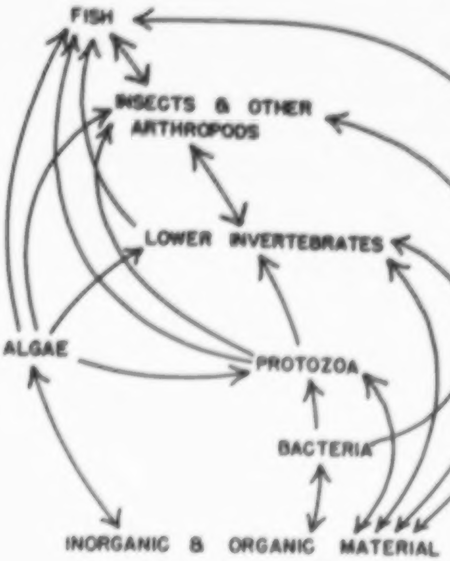

Figure 1: An Aquatic Food Web.

Response of Aquatic Communities to Stress

In any population consisting of various ages, sizes, sexes, etc. of a single species, there will be some individuals that are more sensitive to a particular type of stress than the others. This is true whether the population consists of humans or fish. There is usually a range of concentrations, temperatures, etc. which the organisms will tolerate without any adverse effects. It is important to note that this is true for some very toxic materials such as cyanide, and that the reverse is true for most beneficial substances such as table salt or vitamin A (i.e. unfavorable and even lethal responses). When the concentration or application of the stress increases beyond the point tolerated by the organism, the more sensitive or weaker individuals in the population will begin to respond (in the case of the lethal threshold, by dying). Gradually as the stress increases, more and more members of the population will respond until the entire population is doing so. The important thing is that all organisms, even of a single species, do not respond in the same way to the same level of stress. In practical terms this means that an industrial spill that causes substantial numbers of the population to respond is probably well above the response concentration for the weaker members, and well into the concentration causing a response for the stronger members. Thus nearly the entire population is affected. In general, the amount of stress that affects only a relatively small number of organisms in a population goes unnoticed unless an experienced biologist happens to be gathering data on the situation in question.

The aquatic community which consists of a mixture of species follows essentially the same pattern, that is, the species most sensitive to the stress (which are generally those species living under marginal or suboptimal conditions) disappear while the more resistant individuals may do even better and increase in numbers. This is shown in Figures 2 and 3; notice that the curve in Figure 3 is depressed when one compares it to the curve in Figure 2, but the tail of the curve in Figure 3 is much longer, indicating that a few of the species have done even better than those in Figure 2 once their competitors were partially removed. This is an important characteristic of the response of complex communities because it shows

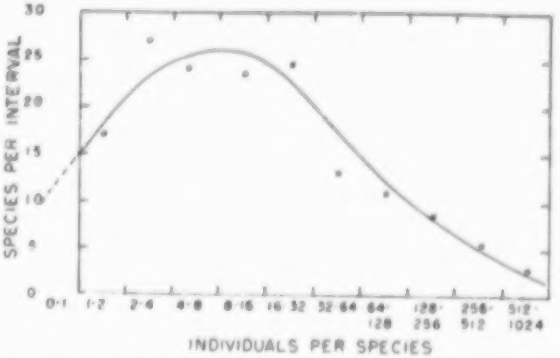

Figure 2: Bar Graphs Showing Population Structure under Different Degree of Pollutional Stress.

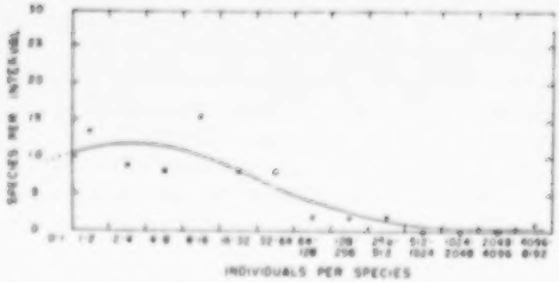

Figure 3: Graph of Diatom Population from a Section of Ridley Creek, Chester County, Pennsylvania, not adversely affected by pollution.

that the initial response to stress may be a change in the complexity of the system (i.e. the number of species), but a compensation mechanism in numbers of individuals may result in about the same biomass being present in each of the two communities. However, the biomass is represented by few species in the stressed community. This means that one has more "eggs in one basket," and any natural event which eliminates one of the high density species in the stressed community is going to have a much more significant effect than the same stress eliminating the same species in an unstressed community. Thus the complex communities are more stable in their performance because complex communities are less affected by the continual replacement of species which is characteristic of the natural successional process.

Most of the species in natural communities are present in relatively low numbers because the competition is keen. However, when pollutional stress removes some of the competition, the survivors become overabundant and then are termed pest species. The dieoffs of one of these overabundant species, even when they consist of algae or other lower life forms, can cause taste and odor problems, clogged filters, lower the oxygen content of the water and otherwise disrupt an aquatic system. The loss of a single species in the diverse low number of individuals per species system, however, is not nearly so disruptive. This, of course, is a rather crude and grossly oversimplified statement of the "balance of nature".

Case History Studies

The response of aquatic communities to spills of hazardous materials can be divided into the immediate response to acute stress; the response to chronic stress from materials with residual toxicity and the recovery response of the community following removal of the stress. The following case history studies of ethyl benzene-creosote, acid, and caustic spills illustrate the response of the various components of the aquatic community to drastically altered environmental conditions. The natural biological recovery following acute stress resulting from the spill of hazardous materials is documented and contrasted in these case history studies.

The Biological Damage and Recovery from an Ethyl Benzene-Creosote Spill

The effect of an abrupt release of acutely toxic material into a river is an immediate stress on the organisms in the river, followed by dilution of the waste and eventual restoration of water quality. A spill of this nature occurred October 10, 1970, at Salem, Virginia, on the Roanoke River. Ethyl benzene mixed with creosote was spilled into the Roanoke River from a primary storage tank of the Koppers Company. Approximately 2,000 gallons of solvent escaped and entered an open cooling water ditch (100 gal/min) which flowed into the Roanoke River. Approximately 400 to 600 gallons of the solvent entered the river in a period of 1 to 2 hours. River flow at the time of the spill was 19,000 gal/min, resulting in an estimated concentration of solvent at the point of discharge of 1,000 ppm. The subsequent fish kill was reported by the Virginia Water Pollution Control Board, and a total of 13,281 fish were killed consisting of 7,979 rough fish and 5,302 sport fish. Initial estimates by the water control board indicated that biological damage extended for a distance of 7 miles below the plant's outfall.

The exact toxicity of the ethyl benzene-creosote mixture is not known. However, using static bioassays, Cairns and Scheier (1959) found that the 96 hour TL_m for *Lepomis macrochirus* (bluegill sunfish) was 10.0 ppm for creosol. Pickering and Henderson (1966) established the 96-hour TL_m for the bluegill using ethyl benzene at 29 ppm under static conditions. The synergistic or antagonistic actions of these compounds, or their action with other compounds in the river could have altered the acute toxicity of the spilled material in the Roanoke River.

Sampling stations were selected above and below the site of the spill and were sampled for both fish and aquatic macroinvertebrates. Sampling was done between 6 and 10 days after the spill for aquatic invertebrates, and 9 to 11 days after the spill for fish. A follow-up bottom fauna and cursory fish survey was conducted April 1 and 2, 1971, (six months later) to determine the extent of recovery. All sites were selected for their ecological similarity, having shallow riffles with rock and gravel beds with heavily wooded banks. The sampling stations were as follows:

Reference Station 1—Located 50 yards above Virginia Rt. 612 Bridge and one-half mile upstream from the spill site.

Reference Station 2—Located adjacent to Koppers Plant and .03 miles upstream from the spill site.

Station 3—Located 0.5 miles below the site of the spill with access via Krogers Road.

Station 4—Located approximately 2.0 miles below the site of the spill with access via Duguid Road.

Station 5—Located 3.5 miles below Koppers with access via Mill Street.

Station 6—Located approximately 4.5 miles below Koppers with access via Union Street.

Station 7—Located approximately 6 miles below Koppers with access via Colorado Street.

Fish Survey

Fish were collected using a 10 foot x 4 foot seine of 1/4 inch mesh. All ecologically distinct sections of the stream were searched for fish at each of the seven sampling stations.

Jordan published a list of fishes taken from several places in and near Salem, Virginia (1890: 120-124). Since then several collectors have sampled the river, including Raney and Ross. In 1952 they made a large and representative collection of the Roanoke River at the Route 11 crossing, on the Montgomery-Roanoke County line (V. P. I. & S. U. #506). There were 33 species in the collection, now preserved in the Cornell University Fish Collection at Ithaca, New York (Table 1). Jordan's results listed 28 species (Table 1). Four of the species obtained by Raney and Ross in 1952 were not recognized by Jordan, those marked with an asterisk. These collections are closely comparable and represented the former stream faunistic composition in the area under study.

Based on the survey of the Roanoke River conducted immediately after the spill, the fish fauna appeared to be in a state of good health except for the portions of the river delimited by Stations 3 and 4 (Figure 4). A total of 26 species of fish were found at Station 1 with 20 species at Reference Station 2. Smallmouth bass, bluegills, and rock bass were present at the reference stations, but were absent at Stations 3 and 4 downstream (Table 2). Six species of perches were present at Reference Station 1, but were absent at Reference Station 2. Their absence was probably due to the introduction of sediments from highway and construction projects located between the two stations. Stations 3 and 4 below the site of the spill had a paucity of fish with only four species of fish (all minnows) being found at Station 3 and eight at Station 4 (Table 2).

At Station 5 approximately three and one-half miles below the Koppers Plant, 23 different species of fish were found, making it comparable to the diversities found at the reference stations. Stations 6 and 7 were highly productive with diversities similar to those found at the reference stations. They also supported a greater biomass of fish than noted at the other stations. This appeared to be due to nutrient enrichment which resulted in stimulated algal growth.

Bottom Fauna Survey

Four Surber Square Foot Samples were taken in a transect across the Roanoke River at each sampling station to quantitatively determine the effects of the spill on the bottom fauna. A bottom net sample was also taken at each station for qualitative evaluation of species diversity. Bottom organisms were separated from the debris using a number 30 mesh sieve and preserved in 70% ethanol for enumeration and identification.

Based on the survey of the Roanoke River conducted October 19-21, 1970, the bottom fauna at Stations 3 and 4 were drastically reduced when compared to Reference Stations 1 and 2. Eighteen taxa of bottom fauna were found at Reference Station 1 with 20 found at Reference Station 2 (Figure 4).

Construction of a sewer line introduced suspended solids between the two reference stations and may have been responsible for the decrease in density at Reference Station 2 (Figure 5). Mayflies, stoneflies, and caddisflies (pollution intolerant organisms) were present at the reference stations, but were absent at Stations 3 and 4 (Table 3).

Stations 3 and 4 located below the site of the spill had a typical "pollution tolerant" community. Pollution tolerant snails and midge larvae made up the major part of the community. Fourteen taxa of bottom fauna were found at Station 3 with 17 found at Station 4. The average number of organisms/ft^2 was lower at these stations when compared to Reference Station 1, probably indicating an additive effect of sedimentation and toxicity from the spill.

Urbanization and the introduction of other industrial discharges into the Roanoke River influenced the character of the benthic communities at Stations 5, 6, and 7. *Cladophara*, a green algae was present at Stations 5, 6, and 7 indicating nutrient enrichment. Twenty taxa of bottom fauna were present at Station 5 with extremely numerous herbivorous caddisfly larvae and snails contributing to the high productivity of the area. Stations 6 and 7 supported a bottom fauna community typical of a nutrient enriched area.

A numerical diversity index evaluation ($\bar{d}$) (Wilhm and Dorris, 1968) indicated that Stations 1, 2, and 4 were healthy stations. All other stations qualified

TABLE 1

Fishes Taken by Jordan in 1888 and by Raney and Ross in 1952
from the upper Roanoke River in Montgomery and Roanoke Counties, Virginia

	Jordan 1888	Raney & Ross 1952
Suckers, family Catostomidae.		
Hog sucker, *Hypentelium nigricans*	common	common
Roanoke hog sucker, *H. roanokense*		common*
Rustyside sucker, *Thoburnia rhothoeca*		several*
Common sucker, *Catostomus c. commersoni*	common	common
Black jumprock, *Moxostoma cervinum*	common	common
Bigeye jumprock, *M. ariommum*		common*
V-lip redhorse, *M. collapsum*		common
Suckermouth redhorse, *M. papillosum*	few	one
Minnows, family Cyprinidae.		
Rosyside dace, *Richardsonius funduloides*	scarce	
Bluehead chub, *Nocomis leptocephalus*	abundant	common
Nocomis sp.		several*
Blacknose dace, *Rhinichthys a. atratulus*	common	scarce
Cutlips minnow, *Exoglossum maxillingua*	common	common
Bluntnose minnow, *Pimephales notatus*		
Silvery minnow, *Hybognathus nuchalis regius*		one
Stoneroller minnow, *Campostoma anomalum michauxi*	common	several
Mountain redbelly dace, *Chrosomus oreas*	abundant	several
Mimic shiner, *Notropis volucellus*		common
Rosefin shiner, *Notropis a. ardens*	common	abundant
Crescent shiner, *Notropis cerasinus*	abundant	abundant
White shiner, *Notropis cornutus albeolus*	common	common
Satinfin minnow, *Notropis analostanus*	common	
Swallowtail shiner, *Notropis procne longiceps*	not rare	common
Spottail shiner, *Notropis hudsonius saludanus*		one
Catfishes, family Ictaluridae.		
Orangefin madtom, *Noturus gilberti*	present	several
Margined madtom, *Noturus insignis*	common	common
Sunfishes, family Centrarchidae.		
Smallmouth bass, *Micropterus d. dolomieui*	scarce	several
Redbreast sunfish, *Lepomis auritus*	common	common
Pumpkinseed, *Lepomis gibbosus*	scarce	
Roanoke rockbass, *Ambloplites rupestris cavifrons*	two	
Rockbass intergrades *A. r. rupestris* x *A. r. cavifrons*		several
Perches, family Percidae.		
Roanoke logperch, *Percina rex*	two	few
Piedmont darter, *Percina crassa roanoka*	common	common
Shield darter, *Percina peltata*	several	several
Fantail darter, *Etheostoma f. flabellare*	common	common
Riverweed darter, *Etheostoma podostemone*	common	common
Johnny darter, *Etheostoma nigrum nigrum*	one	several
Eels, family Anguillidae.		
Common eel, *Anguilla rostrata*	common	

*Species not recognized by Jordan.

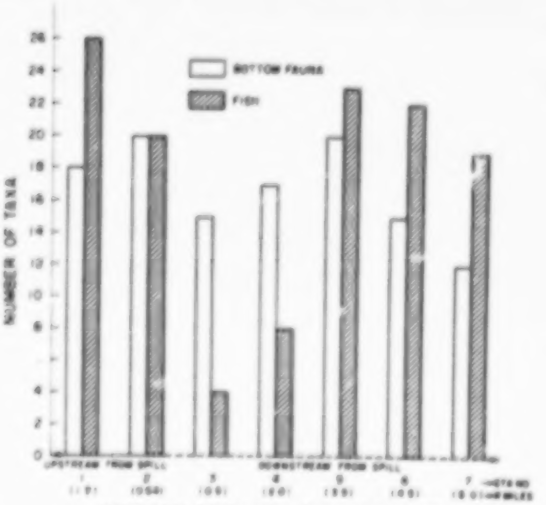

Figure 4: The Number of Bottom Fauna and Fish Found at Each Sampling Station.

as mildly polluted (Figure 6). However, based on density, diversity, taxonomic information and the diversity index evaluations, it appeared that the degradation of the Roanoke River due to the Koppers Company operations and/or spill was restricted to that area extending not more than three and one half miles below the plant.

Recovery Survey

A fish and bottom fauna survey was conducted in early April (approximately six months after the ethyl benzene-creosote spill) to document the extent of recovery of the damaged areas.

The results of the bottom fauna survey showed that riffle beetles which were present at Station 3, 6-10 days after the spill were absent six months later, possibly due to either a residual toxicity from the insoluble creosote or from continued introduction of suspended solids from construction (Table 3). Mayflies and stoneflies had recolonized the affected areas, indicating fairly good water quality since these organisms are generally considered "pollution intolerant" organisms.

A cursory fish survey (six months after the spill) of the upstream and downstream area around the Koppers Plant indicated that:

(1) The upstream area (Reference Station 1) still supported a healthy and diversified fish fauna. Approximately 28 species of fish were present including representatives from the sucker, minnow, catfish, sunfish, and perch families.

(2) The area immediately below the site of the spill supported a suppressed population of fish generally represented by the minnows. Apparently the minnows can reinvade more rapidly or are more resistant to any lingering toxicity or discharges from the Koppers Plant than are the other groups of fish.

SUMMARY

(1) The effects of an acute stress from an industrial spill of ethyl benzene and creosote were to decrease the diversity and density of both the fish and bottom fauna for approximately 3 miles below the site of the spill.

(2) A differential response to the stress was apparent with all major groups of fish except the minnows being entirely eliminated in the stressed area. Perhaps the minnows avoided the stress by swimming into small isolated tributaries or perhaps they rapidly reinvaded the area, or they may be more tolerant to this type of stress.

(3) Mayflies, stoneflies, caddisflies, and mussels did not survive the stress and were eliminated. However, mayflies and stoneflies were present six months later indicating improved water quality.

(4) Riffle beetles, trueflies, crayfish, some snails, and segmented worms were apparently able to survive the short term exposure to the ethyl benzene and creosote stress.

The Biological Damage and Recovery of the Clinch River Following Acute pH Stresses

The Clinch River has been subjected to two major industrial spills which have resulted in fish kills and elimination of other aquatic organisms. To evaluate the effects of these spills and to study the recovery processes, benthic organisms and fish have been collected from the Clinch in southwestern Virginia and northeastern Tennessee for two years.

Description of the Clinch River

The Clinch River is a headwater tributary of the Tennessee River located in the ridge and valley region of southwestern Virginia and eastern Tennessee. As the main tributary of the Clinch River Basin, the Clinch drains 1,260 square miles of land in Virginia and extends for a distance of 148 river miles before it enters Tennessee (Tackett, 1963). The average discharge for the Clinch at Speer's Ferry, Virginia, during the period of 1920 to 1960 was 1,578 c.f.s. with a maximum of 45,300 c.f.s. noted in January, 1957, and a minimum of 42 c.f.s. noted in September, 1939 (U.S. Geological Survey, 1960).

As the Clinch passes through the mountainous regions of Virginia it flows over exposed geologic formations of limestone and dolomite which range in age from early Cambrian to Pennsylvanian (Cooper, 1945). These formations contribute cal-

TABLE 2

The numbers of fishes collected at 7 stations (pagell) from the Roanoke River on October 19-21, 1970 in Roanoke County and Salem, Virginia.

Stations:	1	2	3	4	5	6	7
Suckers, family Catostomidae							
Hog sucker, *Hypentelium nigricans*	3	20		2	7	11	14
Rustyside sucker, *Thoburnia Hamiltoni*	12	10		2	1	14	7
Common sucker, *Catostomus c. commersoni*		1			1		
Black jumprock, *Moxostoma cervinum*	16	12		1		1	18
Bigeye jumprock, *Moxostoma ariommum*	2	8			2	6	6
V-lip redhorse, *Moxostoma collapsum*	4	4			6	1	2
Suckermouth redhorse, *Moxostoma papillosum*		1			1		
Minnows, family Cyprinidae							
Bluntnose minnow, *Pimephales notatus*	36	15			3	4	
Bluehead chub, *Nocomis leptocephalus*	10	13	2	4	4	21	20
Nocomis sp.		8				10	35
Cutlips minnow, *Exoglossum maxillingua*	1						
Silvery minnow, *Hybognathus nuchalis regius*	1						
Stoneroller minnow, *Campostoma anomalum michauxi*	15	69			10	54	42
Mountain redbelly dace, *Chrosomus oreas*					1		
Rosefin shiner, *Notropis a. ardens*	86	151	3	15	8	144	142
Crescent shiner, *Notropis cerasinus*	126	77	19	47	15	64	29
White shiner, *Notropis cornutus albeolus*	125	8	4	46	109	50	76
Satinfin shiner, *Notropis analostanus*	1	1			1	7	1
Swallowtail shiner, *Notropis procne longiceps*						35	3
Spottail shiner, *Notropis hudsonius saludanus*		1			4		
Catfishes, family Ictaluridae							
Orangefin madtom, *Noturus gilberti*	1						
Margined madtom, *Noturus insignis*	17	24		1	8	8	16
Sunfishes, family Centrarchidae							
Smallmouth bass, *Micropterus d. dolomieui*	2				2		
Bluegill, *Lepomis m. macrochirus*		2			2		
Redbreast sunfish, *Lepomis auritus*	7	2			3	6	
Pumpkinseed, *Lepomis gibbosus*	1						
Rockbass intergrades, *Ambloplites r. rupestris* x *A. r. cavifrons*	1	2			1		1
Perches, family Percidae							
Roanoke logperch, *Percina rex*	15				1	1	2
Piedmont darter, *Percina crassa*	58				35	88	61
Shield darter, *Percina peltata*	1						
Fantail darter, *Etheostoma f. flabellare*	9				1	66	12
Riverweed darter, *Etheostoma podostemone*	7				7	34	18
Johnny darter, *Etheostoma n. nigrum*	2					1	

cium bicarbonate to the water and raise the pH of the river to 8.0-8.5. Because of the high alkalinity, acid discharges from coal mines are readily neutralized. However, discharges from coal washing operations cause a major sedimentation problem in the Guest River and Dump's Creek, two of the larger tributaries of the Clinch.

1967 Fly Ash Pond Spill

The first fish kill occurred when the dike surrounding a fly ash holding pond collapsed at Appalachian Power Company's 700-megawatt steam power generating plant near Carbo, Virginia. At this power plant native coal is utilized to produce steam which is used in the production of electrical power. Because the coal has a high ash content, approximately 960 tons of fly ash is produced daily. To efficiently remove such large quantities of ash from the furnace hoppers, water from the Clinch River is mixed with the ash to form a slurry. This mixture is pumped to large settling lagoons where the ash settles and the supernatant is recycled. Because of recycling, free lime (CaO) in the fly ash

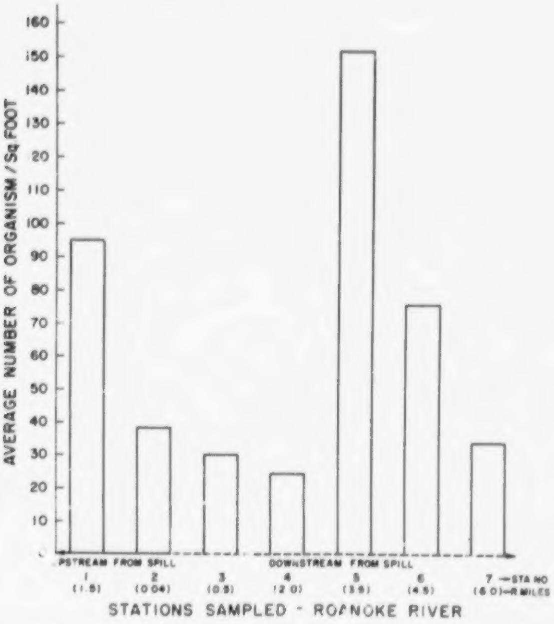

Figure 5: The Average Number of Bottom Fauna/Square Foot at Each Sampling Station.

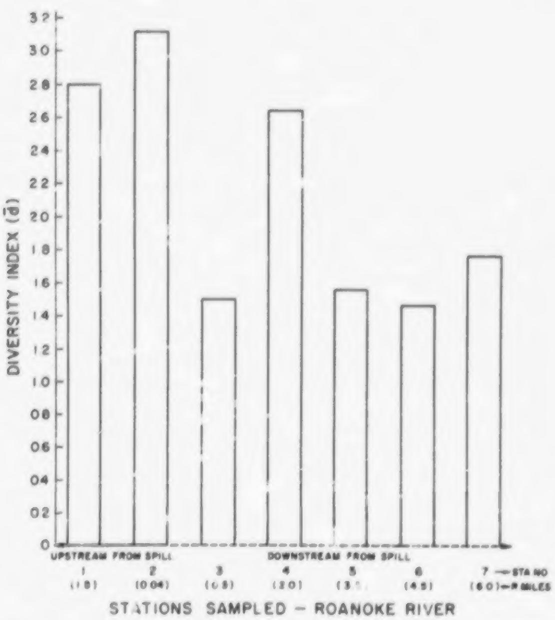

Figure 6: The Diversity Index d for Bottom Fauna at Each Sampling Station.

TABLE 3

Number of Bottom Fauna Genera in Each Family by Stations

	Station No.								
	Six Days After Spill							Six Months After Spill	
Bottom Fauna	1	2	3	4	5	6	7	1	3
	Upstream		*Downstream*					*Upstream*	*Downstream*
Bettles	4*	3	3	2	4	2	2	2	0
Caddisflies	3	3	0	2	2	1	1	2	0
Damselflies	0	0	1	0	0	0	1	0	0
Dobsonflies	1	1	1	2	2	2	1	1	1
Mayflies	3	5	0	3	2	2	3	5	5
Stoneflies	1	1	0	1	1	0	0	2	2
Trueflies	4	3	2	3	4	2	1	1	2
Crayfish	1	1	1	1	1	0	1	1	0
Scuds	0	0	0	0	0	0	1	0	0
Sowbugs	0	0	0	1	0	0	0	0	0
Flatworms	0	0	1	0	0	0	0	0	0
Mussels	1	1	0	0	1	0	0	0	0
Snails	1	1	3	2	2	2	1	1	1
Worms	1	1	1	1	1	1	1	0	0
Total Number	20	20	13	18	20	12	13	15	11

*Number of Genera

reacts with water to form $Ca(OH)_2$. This gradually raises the pH of the recirculating water and the water in the fly ash lagoons to extremely high pH values ranging from 12.0 to 12.7 (Anonymous, 1967b).

In June 1967, a 50–75 foot section of a dike surrounding one of the fly ash settling lagoons failed. Within less than an hour 400 acre feet (approximately 130 million gallons) poured into Dump's Creek, which joins the Clinch River 0.5 miles downstream. This caustic slug equalled 40% of the daily flow of the Clinch at the time and resulted in blocking the normal flow for several minutes. It also raised the water level several feet and forced some of the waste approximately 0.5 miles upstream.

For four and one-half days following the spill the alkaline slug traveled downstream at a rate of approximately 0.85 miles an hour killing essentially all the fish in its path (Anonymous, 1967b). During this period 162,000 sport and rough fish were killed in 66 miles of the Clinch River in Virginia. An additional 54,600 sport and rough fish were killed in 24 river miles in Tennessee until the polluted mass was diluted, dispersed, and neutralized in the river by natural physical-chemical forces. The chemical reactions involved in neutralization were:

1) $Ca(OH)_2 + Ca(HCO_3)_2 \dashrightarrow 2CaCO_3 + 2H_2O$

In addition CO_2 from the atmosphere reacted with the water to form:

2) $H^2O + CO_2 \rightleftharpoons H_2CO_3$

3) $Ca(OH)_2 + H_2CO_3 \dashrightarrow CaCO_3 + 2H_2O$

The lethal agent was reported to have been the high pH of the alkaline water which was composed of 90% hydroxide alkalinity and 10% carbonate alkalinity. A secondary effect which may have contributed to the biological damage was a depression in the dissolved oxygen concentration caused by the decaying organic matter (Anonymous, 1967b).

Ten days after the collapse of the dike the Virginia State Water Control Board conducted a bottom fauna survey at selected stations above and below the site of the spill to assess damage to the benthic fish food organisms (Anonymous, 1967a). They observed that:

1) Bottom dwelling fish food organisms appeared to have been completely eliminated for a distance of approximately 3 or 4 miles below the site of the spill (Figures 7 & 8).

2) A drastic reduction in the number and kinds of bottom dwelling fish food organisms occurred in the Clinch River for 77 miles below the spill (Figures 7 & 8).

3) Snails and mussels were eliminated for 11.5 miles below Carbo, Virginia.

4) The Virginia State Water Control Board, based on past experience, predicted that as far as total weight per square foot of stream bottom, the Clinch River would recover to its former productive capacity within three months after the spill. Both the Virginia and Tennessee Game Commissions believed that the stream organisms would appear in sufficient numbers for fish restocking in the fall of 1967 (Anonymous, 1967a).

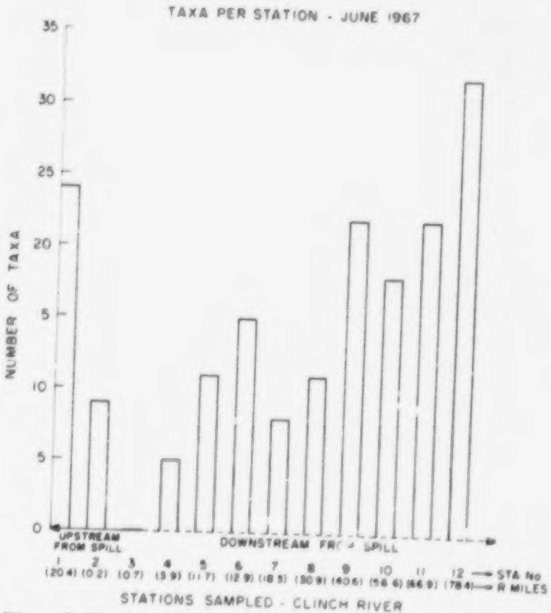

Figure 7: Number of Taxa Found at Each Station for June, 1967 Bottom Fauna Survey.

Materials and Methods

During the summer and fall of 1969, a bottom fauna and fish survey of the Clinch River was conducted to study the extent of the biological recovery of the river following the 1967 fly ash spill. Particular emphasis was placed on studying the bottom fauna communities above and below the spill site because:

1) Benthic organisms are relatively sessile organisms and they cannot quickly avoid environmental stresses as fish often are able to do;

2) They have rather long and complex life histories and their presence or absence reflects the history of the environment,

3) Since they are members of the food web in an aquatic environment, their presence or absence directly effects fish populations;

4) Sampling techniques for bottom fauna are more reliable than techniques for fish; and

5) More biological information can be gained from studying this group of organisms per dollar invested than any other group.

The bottom fauna survey involved the locating and sampling of twenty-one ecologically similar stations which extended from Blackford, Virginia, to Sneedville, Tennessee, a distance of 120 river miles (Figure 9). Four stations were located above the site of the spill to serve as reference or control stations with which downstream stations could be compared. Twelve stations were located below the spill site to assess the river's recovery and to evalu-

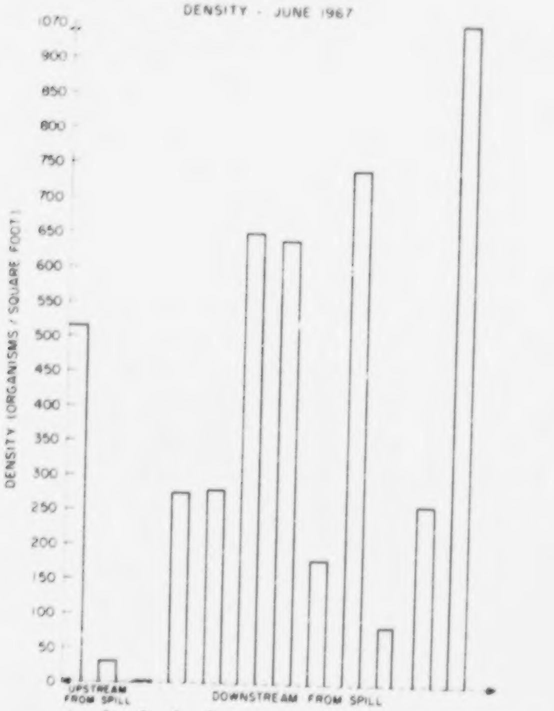

Figure 8: Density of Organisms Found at Each Station for June, 1967 Bottom Fauna Survey.

ate any contributing influences arising from industries, municipalities, or agricultural areas. Five additional stations were established on tributaries with pollution sources which could have effected the main river stations.

Sampling sites with comparable habitats and ecological similarity were selected so comparisons could be made between stations. After locating the stations, sampling was accomplished using a Turtox 8″ × 10″ × 18″ rectangular bottom net and a Surber square foot sampler. Care was taken that an equal collecting effort was made at each station. Each station was divided into three substations (left bank, right bank, and midchannel), and samples were taken from each substation with a bottom net since it had been observed that waste discharges were often restricted to certain portions of the river after discharge. Five Surber samples were taken along a transect through the riffle area for quantitative information. Immediately after collection, all samples were passed through a series of graded sieves (Tyler mesh Nos. 4, 10, and 35) and the organisms were removed and preserved in 70% ethanol for later identification and enumeration.

Fish samples were collected using a 10′ × 4′ seine of 1/4 inch mesh. All specimens were preserved in formalin and stored in 70% alcohol in the Virginia Polytechnic Institute and State University museum. The collections were obtained at two stations above

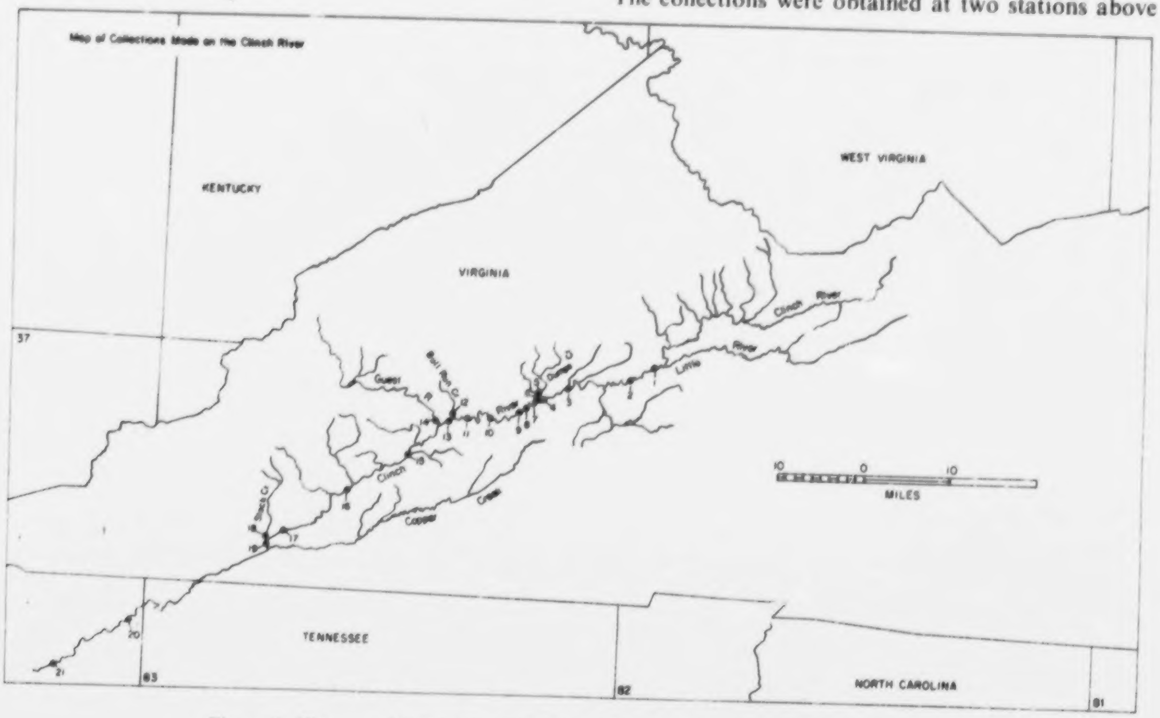

Figure 9: Diagram of Sampling Locations on Clinch River and Related Tributaries.

the spill site and at four stations below. Only the shallow areas and riffles were sampled.

Results and Discussion

The number of bottom fauna taxa found at each station are summarized in a histogram, Figure 10. A difference existed between upstream reference stations and stations immediately below the spill site for a distance of approximately 18 miles. At Reference Stations 1 through 4 the number of taxa varied between 48 and 54, while below the spill site there was a decrease at Station 7 to 43 taxa followed by an even more pronounced decrease at Station 8 to 33. This low value was followed by an increase in the number of species at the next three stations until at Station 11 there were 46 taxa, approximately the same number as were observed at the reference stations. At Station 13 a decrease in the number of species was found, followed by an increased number of species equal to reference station values at the remaining downstream stations.

In Figure 11, a graph of density which includes all snail and freshwater mussel species, the difference between the upstream reference stations and stations below the spill site was even more pronounced. Densities for the reference stations ranged between 145.2 and 24.6 organisms per square foot. In contrast, densities at Stations 8-11 varied between 2.4 and 18.8 organisms per square foot with the highest density being found at Station 11, the station located furthest downstream. Station 13 showed a reduction in density which appeared to be due to unsuitable substrate conditions for benthic colonization and the influence of the tributary that flows into the Clinch River just above this station.

Figure 12, a graph of density which does not include snails and mussel species, indicated a difference between Reference Stations 1-4 and Stations 7-11. In addition, Figure 12 also indicated that:

1) There was a reduction in the densities at Stations 1-4 and 13-21 when compared to the same stations in Figure 4. This was caused by the exclusion of the snail and mussel data, since these groups made up large portions of the invertebrate community at each station.

2) Densities were not affected by excluding snail and mussel species at Stations 7-11 because molluscs had not become reestablished after the spill. This may be the result of reduced susceptibility to downstream drift when compared to the drift found for insect larvae and other invertebrates, longer life

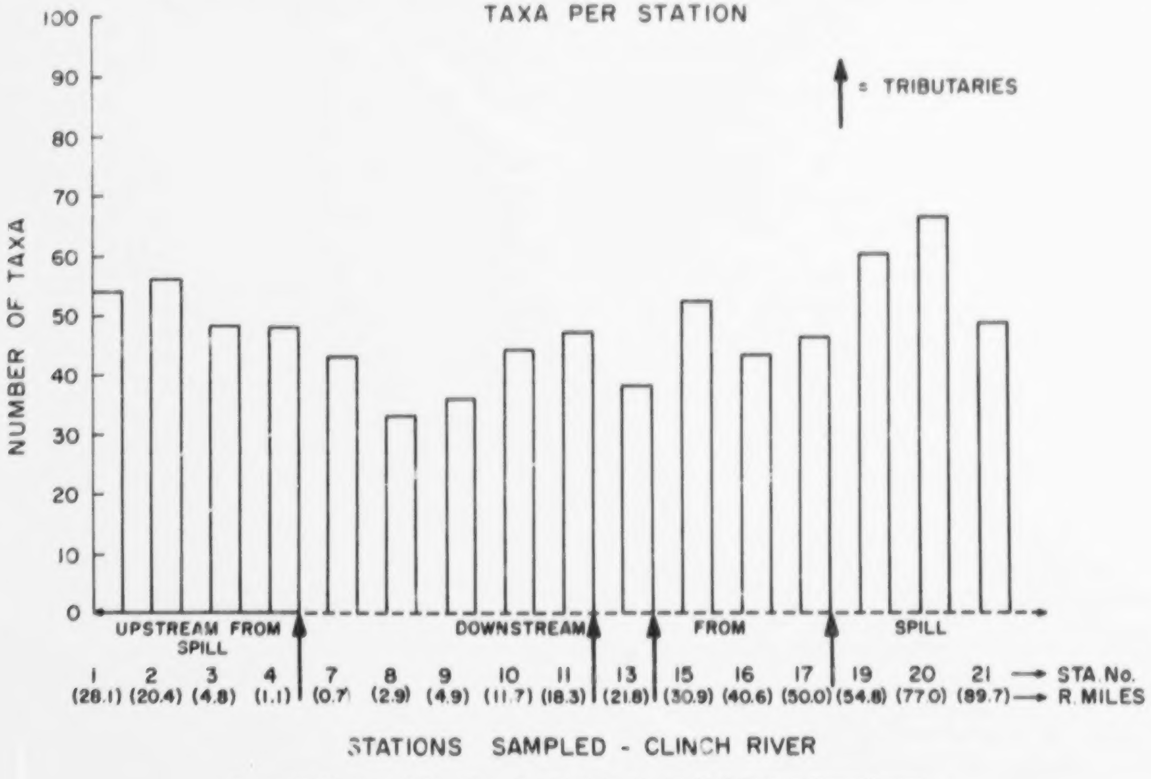

Figure 10. Number of Taxa Found at Each Station for 1969 Bottom Fauna Survey.

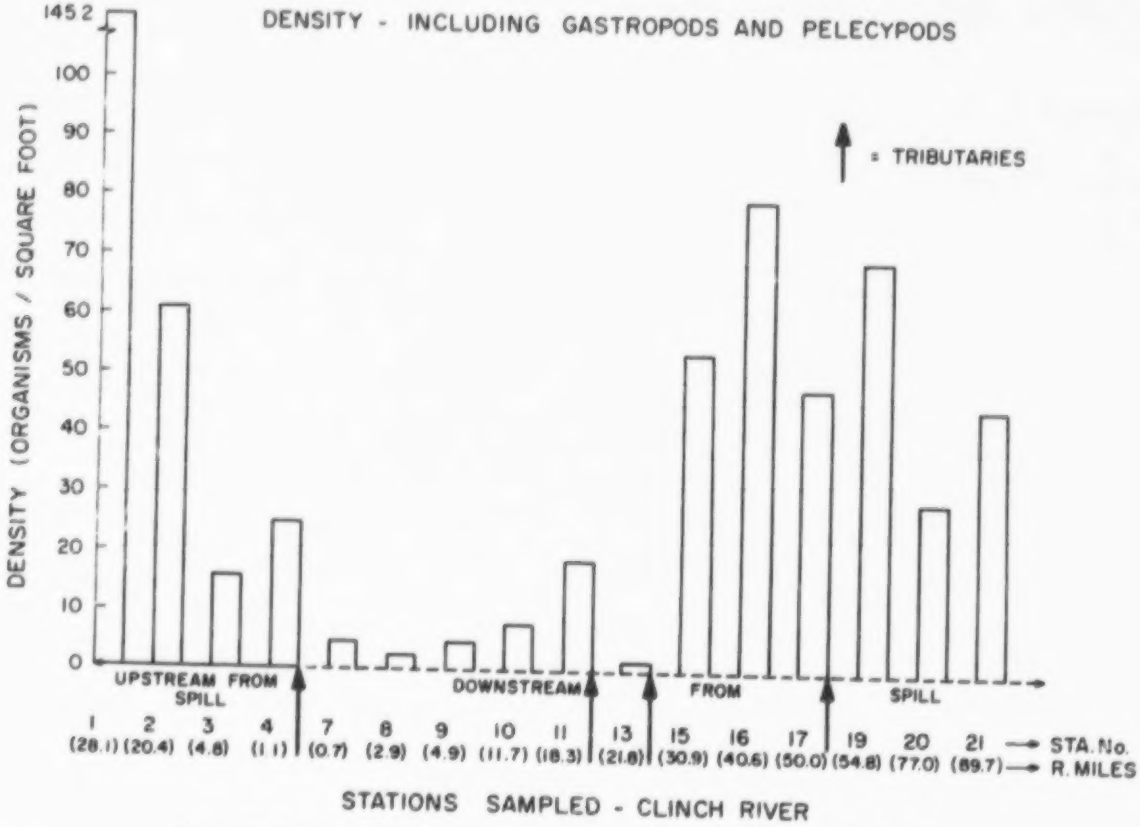

Figure 11: Density of Organisms, Including Molluscs, at Each Station for 1969 Survey.

cycles than found for most other aquatic invertebrates, and the lack of an aerial stage in their life cycles, all of which would affect their rate and extent of recolonization.

The differences found in diversities and densities at Stations 7-11 indicate a possible recovery pattern. This pattern would involve a combination of interrelated factors which would include the amount of damage at each station from the spill, differing rates of recolonization by different organisms, and a continuing mild environmental stress upon a limited portion of the aquatic ecosystem being studied.

The continuing environmental stress appears to have been caused by a discharge from the Appalachian Power Company's plant above Station 7. This discharge channeled along the right bank for some distance before mixing, and although it did not affect the overall diversity found at Station 7, it did appear to have an adverse effect upon aquatic organisms at downstream stations.

Community structure analyses of the bottom fauna collected at each of the sixteen sampling stations located on the Clinch River indicated that the bottom fauna community structures at stations below the spill site were similar to the control stations upstream (Table 4). In this study diversity ($\overline{d}$) was calculated for the left bank, right bank, and midchannel substations for all sixteen stations on the Clinch River using the following equation:

$$d = \Sigma \ (Ni/N) \log_2(Ni/N)$$

A complete explanation of this technique is given by Wilhm and Dorris (1968).

"Clean water" areas have been found by Wilhm and Dorris (1968) to have $\overline{d}$ values exceeding 3.0. Border line values such as were found at the right bank substation at Station 7, left bank substation at Stations 1 and 21, and the midchannel substation at Stations 17 and 20 indicate areas of moderate pollution. However, it appears that the Clinch River has substantially recovered from the fly ash pond spill when the community structure of the bottom fauna is used as a criterion.

Results for the fish collections are given in Figures 13 and 14. Figure 16 gives the number of different fish species, made up mostly of minnows and darters, found at each station. Reference Stations

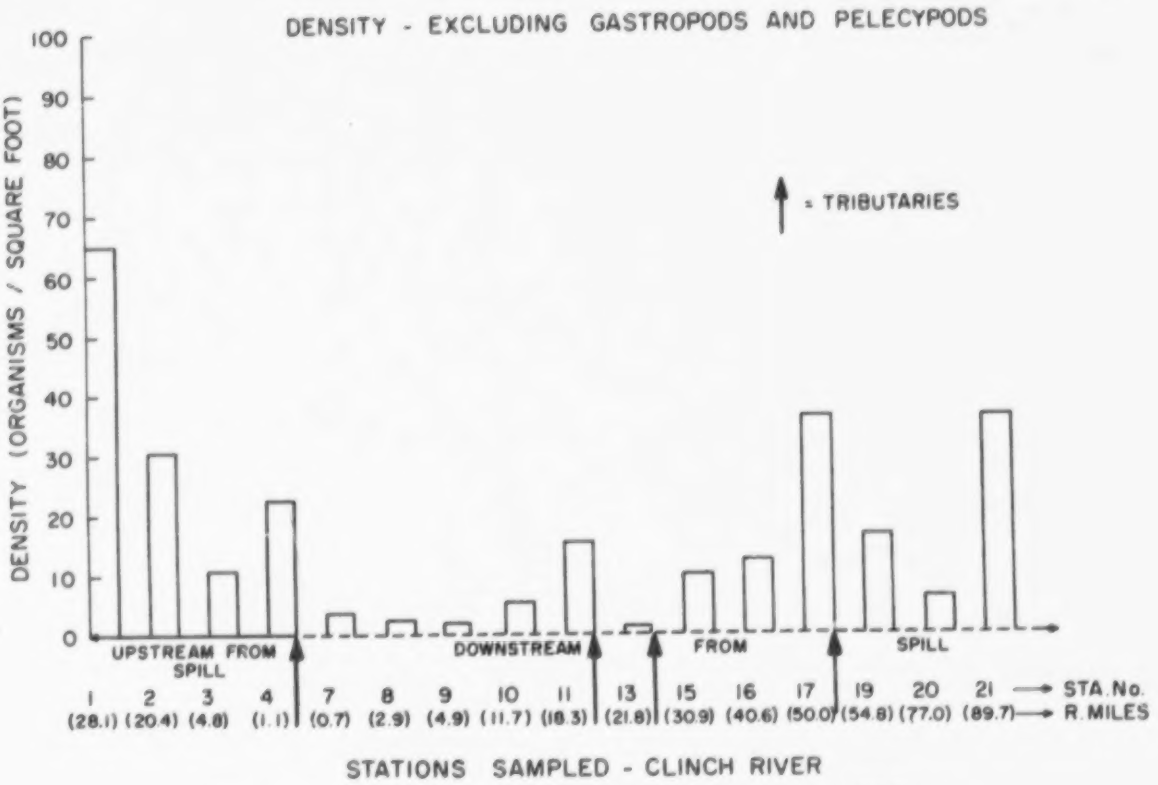

Figure 12: Density of Organisms, Excluding Molluscs, at Each Station for 1969 Survey.

TABLE 4

Diversity Values Obtained with the Index $\overline{d} = - \Sigma (Ni/N)\log_2(Ni/N)$ for Bottom Fauna Collected at Stations Sampled on the Clinch River

Substations	Stations																			
	Above Spill				Below Spill															
	1	2	3	4	7	8	9	10	11	13	15	16	17	19	20	21
Left Bank	2.97	3.65	3.75	3.79	4.21	4.35	3.76	3.29	3.61	3.81	3.95	3.85	3.67	4.19	4.19	2.98
Midchannel	3.22	3.33	3.27	3.93	3.28	3.64	2.88	3.19	4.17	3.64	3.26	3.30	2.48	3.41	2.26	3.37
Right Bank	3.32	3.86	3.94	4.03	2.92	4.06	4.01	4.06	3.87	4.01	3.86	3.31	3.79	3.54	4.03	3.27

1 and 2 had 19 and 17 different species respectively, while Station 7 below the spill site had 11 species. This difference may be attributed to the decreased availability of fish food organisms and/or the power plant's waste discharges. Further downstream at Station 9 the number of taxa had increased to the same level as observed at the upstream control stations, but a drop at Station 11 to 2 taxa was found. Field observations made at the time of collection showed a large amount of silting at Station 11 which may have caused the reduction in diversity.

Fish densities for each station, Figure 14, showed the same variations as were noted for the bottom fauna—a reduction in density immediately below the spill site followed by an increase the farther downstream the samples were taken.

CONCLUSIONS

From the preliminary survey, conducted two years after the alkaline fly ash pond spill, the following tentative conclusions seem justified:

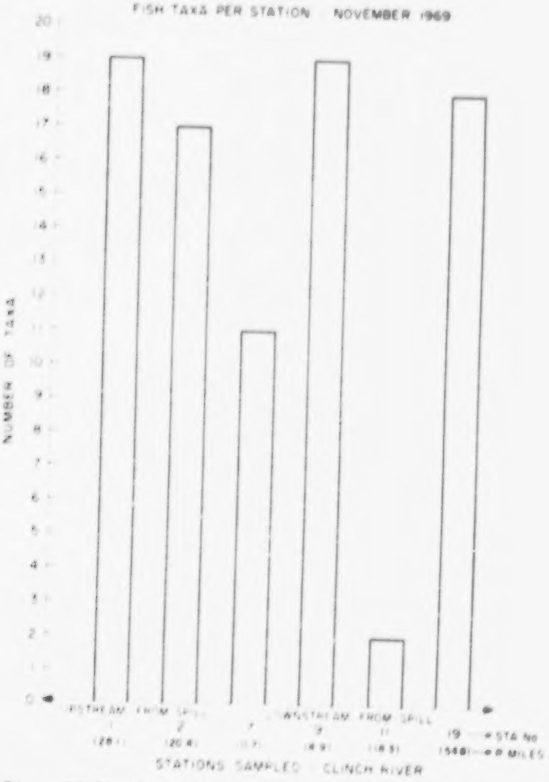

Figure 13: Number of Fish Taxa Found at Sampling Stations for November, 1969 Survey.

1) Aquatic communities of bottom fauna that were completely eliminated below the power plant at Station 7 had recovered to the point where the number of different kinds of organisms found at this station were approximately the same as found at upstream reference stations unaffected by the spill.

2) Communities of benthic organisms at Station 8-11 indicate a linear recovery pattern; i.e. the farther downstream the station is located the higher the density and diversity values.

3) Large portions of the communities at the reference stations and at stations 30 miles or farther downstream from the plant consisted of molluscs. However, these aquatic invertebrates had not recovered at Station 7-11 below the site of the spill. This failure to recolonize appeared to be due to their inherent inability to reinvade and recolonize areas below the spill site as fast as aquatic insects.

4) Community structure analyses indicated that benthic communities below the site of the spill were similar to those found at stations above the spill site and were characteristic of "clean water" situations as defined by Wilhm and Dorris (1968).

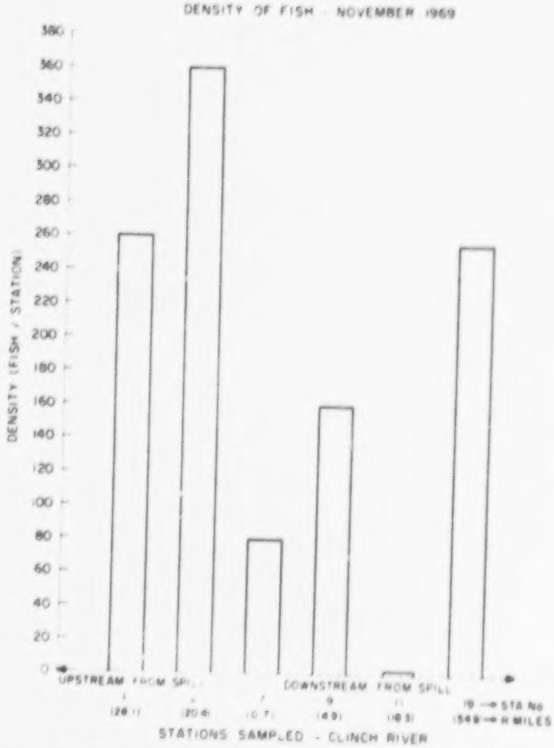

Figure 14: Density of Fish at Each Sampling Station for November, 1969 Survey.

5) Different species of minnows and darters had recolonized stations below the plant, but had not attained the density levels found at upstream reference stations.

6) Two years after the spill, the Clinch River had not fully recovered. However, fish food organisms such as mayflies, stoneflies, hellgrammites, and midge larvae were present at all the areas affected by the spilll and should support a productive sport fishery.

1970 Acid Spill

While undertaking the second year's bottom fauna survey a second industrial spill occurred at the Appalachian Power Plant on June 19, 1970, just after benthic samples had been collected at six stations above the plant and at four stations below. This spill involved the release of an undetermined amount of sulfuric acid which killed approximately 5,300 fish. Cursory examinations by representatives of the Virginia State Water Control Board indicated that stream damage began approximately one mile below the power plant and extended a distance of 13.5 river miles downstream to St. Paul, Virginia (Soukup, 1970).

Materials and Methods

Immediately after notification of the spill a series of cursory examinations were made on the bottom fauna, using the same collecting techniques as previously described, to determine the extent of the damaged area. These examinations were followed by thorough sampling of the stations in the affected area (as delimited by the cursory examinations) and were continued at two week intervals for the next sixty days. Additional samples were collected every four weeks at three unaffected stations during the same period. In all, seven ecologically comparable stations were included in the survey, consisting of one reference (control) station, four stations in the affected area, and two delimiting stations. Station No. 4, located 1.1 river miles above the power plant, served as the upstream reference station with which the affected stations were compared. Stations Nos. 7, 8, 9, and 10, located below the spill site, were located to assess the effects of the spill and to follow the restoration of the damaged ecosystem. Two delimiting stations, Stations Nos. 11 and 13, were established 6.6 and 10.1 river miles below Station No. 10 to verify whether or not the effects of the spill were restricted to that section of the river from Carbo to St. Paul, Virginia.

Results

The total number of organisms found at each station were calculated and plotted (Figure 15). The data from Stations 4, 11, and 13 indicated that these stations were unaffected by the spill. However, seasonal variations did exist as evidenced by the increase in the number of organisms in July, the second sampling period, and the decrease in the number of organisms in August during the third collecting period. At Stations 7-10, the low pH shock caused an immediate decrease in the number of organisms. This was the result of the elimination of all mayfly and mollusc species and reductions in the number of organisms per species for all other species except hellgrammites and adult beetles. The hellgrammite and adult beetle species appeared to have been unaffected by the pH shock.

Two weeks after the spill, the third sampling period, there were increases in the number of organisms/station at Stations 7-10. These increases were probably the result of population development by species that had survived the spill, since new species were rarely found at any of the stations. By the fourth sampling period, four weeks after the spill, organisms which probably arrived by stream drift became more abundant, making up between 4 and 10% of the total number of organisms. They would have made up a larger percentage had it not been for the three genera, *Hydropsyche* sp., *Cheumatopsyche* sp., and *Simulium* sp. Since these organisms are vertically distributed in the substrate (Coleman and Hynes, 1970), it was felt that their population increases were probably due to development of egg masses and immature forms located deep in the substrate which were unaffected by the low pH shock. The eclosion of these immatures would account for the extremely high numerical values found for the fourth sampling period. After the rapid increase in the number of benthic organisms, a stabilization period followed as values decreased and remained fairly stable during the fifth and sixth sampling periods.

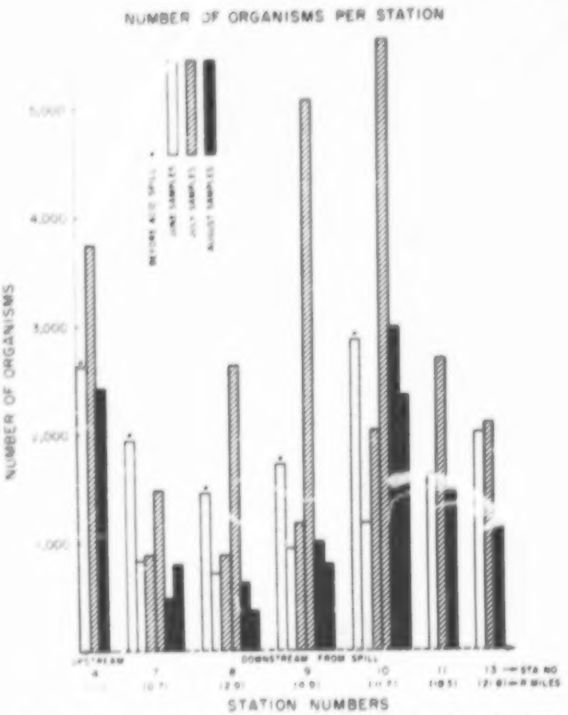

Figure 15: Number of Organisms Per Station for June 19, 1970 Acid Spill.

Community structure analyses were run on the combined collections from each station using the technique developed by Wilhm and Dorris (1968). The results of this evaluation, expressed as diversity indexes ($\bar{d}$), were plotted to form a histogram (Figure 16). Stations sampled before the spill, denoted by an asterisk, had $\bar{d}$ values either above 3.0 or within 0.08 of that figure indicating "clean water" areas (Wilhm and Dorris, 1968). However, a moderately stressed situation was indicated since diversity indices were lower at Stations 8, 9, and 10 when compared to Reference Station No. 4. These reduc-

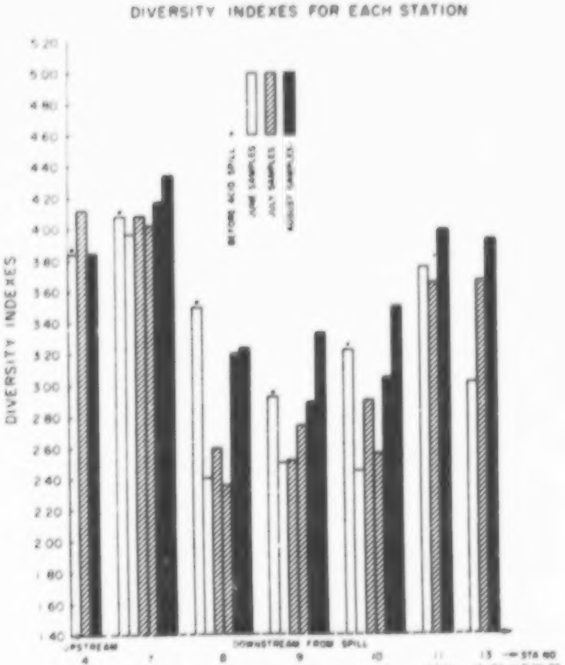

Figure 16: Diversity Indexes for Each Station for the June 19, 1970 Acid Spill.

tions were probably the result of a combination of interrelated factors which may include stream damage from the previous fly ash pond spill and continued discharges from the power plant. Station 7 did not show a decrease because effluents from the power plant were confined to the right side of the river and did not affect the station's overall community structure of aquatic organisms. Biological recovery from the previous alkaline spill also appeared to be further advanced at this station than at Stations 8-10.

After the acid spill, diversity indices at Stations 8, 9, and 10 dropped to between 2.40 and 2.50, indicating that the community structure of the benthic organisms had been altered and were characteristic of streams with moderate pollution (Wilhm and Dorris, 1968). The reduction in $\bar{d}$ values was the result of decreased diversities (i.e. number of different species found) at each station. The number of taxa dropped from an average of 49 to 30 for the three stations, with the largest decrease occurring at Station 9 which had 48 taxa before the spill and 25 after.

Two weeks after the spill, the third sampling period, diversity values began to increase. This pattern of increased $\bar{d}$ values with time continued at Station 9 during the fourth sampling period, but was disrupted at Stations 8 and 10 where values decreased. At these stations disproportional population increases by *Simulium* sp., *Hydropsyche* sp., and *Cheumatopsyche* sp. altered the overall community structure and reduced diversity indices. By the fifth sampling, six weeks after the spill, these organisms were reduced in numbers and $\bar{d}$ values increased to above 3.0 or within 0.11 of that value, showing that the invertebrate communities at each station were within the same "clean water" range as noted before the spill. Diversity values for sampling period six were all above 3.0, indicating stream recovery using community structure analyses.

Diversity values were also calculated for each substation sample and Surber sample at each station. These indices were tabulated along with the values previously mentioned for the combined collections by station number, and comparisons were made between values for each station and between the different stations (Table 5). Examination of indices showed very little difference between the numerical values of the combined samples and the substation and Surber samples, except at Stations 7 and 8. At these stations d values were consistently lower for the right bank substation because of the power plant's effluent which channeled along the right bank before becoming completely mixed.

Relative frequencies of organisms were calculated and plotted for each station, Figure 17. The frequency values were obtained by dividing the number of organisms of a group, tolerant or nontolerant, by the total number of organisms at the station. The tolerant and nontolerant classifications were determined by comparison of samples before and after the spill. If an organism was present in significant numbers before the spill and absent afterwards, it was considered a nontolerant species and vice versa. In this graph the differences between Stations 8-10 and Reference Control Stations 4, 11, and 13 are more obvious. At Stations 4, 11, and 13 the frequencies for nontolerant species were between 30 and 60% during the entire sampling period. At stations 8-10 nontolerant species made up less than 25% of the total population before the acid spill because of the power plant's discharges and incomplete recovery from the alkaline spill. After the acid spill nontolerant organisms were almost completely eliminated at each station. Two weeks later, the third sampling period, they began to recover and continued to do so until the sixth sampling period when frequencies of 20, 22, and 50% were noted for the respective stations.

CONCLUSIONS

The following observations were made after comparing benthic samples collected before and after the June 19th acid spill.

TABLE 5

Diversity Values Obtained with the Index
$\bar{d} = -(Ni/N)\log_2(Ni/N)$
for Bottom Fauna Collected after the
June 19, 1970, Acid Spill on the Clinch River

Station Number	Date	Collection	Left Bank	Midchannel	Right Bank	Surber
4	6-17-70	3.84	4.22	3.44	3.86	3.16
4	7-21-70	4.12	3.80	3.93	4.27	3.17
4	8-15-70	3.84	3.71	3.59	3.63	3.46
7	6-12-70	4.08	4.26	3.73	3.32	3.49
7	6-23-70	3.97	3.93	3.52	3.15	3.75
7	7-7-70	4.07	4.03	3.62	2.42	3.46
7	7-20-70	4.02	3.73	3.41	2.91	3.61
7	8-5-70	4.17	3.74	3.95	1.55	3.65
7	8-16-70	4.34	4.00	3.98	3.51	3.73
8	6-18-70	3.50	3.53	3.67	3.34	2.34
8	6-23-70	2.40	2.11	2.47	2.09	1.77
8	7-8-70	2.59	2.51	2.24	2.49	2.05
8	7-21-70	2.36	2.67	2.39	1.85	2.32
8	8-6-70	3.20	3.01	2.97	3.15	2.25
8	8-16-70	3.23	2.88	3.00	2.85	2.81
9	6-18-70	2.92	3.94	2.83	3.80	2.17
9	6-24-70	2.50	2.41	2.54	2.04	1.70
9	7-8-70	2.51	2.96	2.23	1.64	1.84
9	7-22-70	2.73	2.43	2.69	2.66	2.58
9	8-6-70	2.89	3.06	2.30	2.56	2.57
9	8-17-70	3.33	3.40	2.95	3.23	3.20
10	6-19-70	3.23	3.69	3.04	2.96	2.48
10	6-24-70	2.45	3.01	1.96	2.45	2.05
10	7-9-70	2.90	2.65	3.10	2.64	2.55
10	7-23-70	2.55	2.49	2.36	2.73	2.32
10	8-7-70	3.04	2.78	2.57	3.06	3.23
10	8-17-70	3.50	3.50	2.93	3.21	3.22
11	6-22-70	3.74	3.55	3.51	3.63	3.01
11	7-23-70	3.65	3.24	3.51	3.22	3.47
11	8-18-70	3.98	3.64	3.66	3.91	3.90
13	6-25-70	3.01	3.66	2.28	3.29	2.78
13	7-24-70	3.66	3.96	3.26	3.40	3.19
13	8-18-70	3.91	4.45	3.39	3.90	3.71

(1) Aquatic communities of mayfly and mollusc species were completely eliminated by the low pH shock for a distance of 11.7 river miles. Reductions in the number of individuals per species were also noted for all other species except hellgrammites and beetles which appeared tolerant of the acid shock.

(2) Community structure analyses indicated that the stream invertebrate communities were altered by the acid spill and were characteristic of streams with moderate pollution.

(3) By the fifth sampling period, six weeks after the spill, diversity values were within the same clean water range as noted before the spill.

(4) The relative frequencies of organisms non-tolerant of the pH shock were still increasing by the end of the sampling period.

(5) Sixty days after the acid spill the river had recovered to the point that representative species of aquatic insects found before the spill were present at all the affected stations. Mollusc species were slower to recolonize and had still not recovered by the end of the summer.

SUMMARY

From the four case 'history studies' presented it appears that the biological recovery of damaged rivers is a function of the physical, chemical, and biological characteristics of the receiving stream, the severity and duration of the stress, and the availability of undamaged areas to serve as sources for recolonizing organisms.

Short term acute stresses produced by the release of acidic or caustic materials into a receiving stream

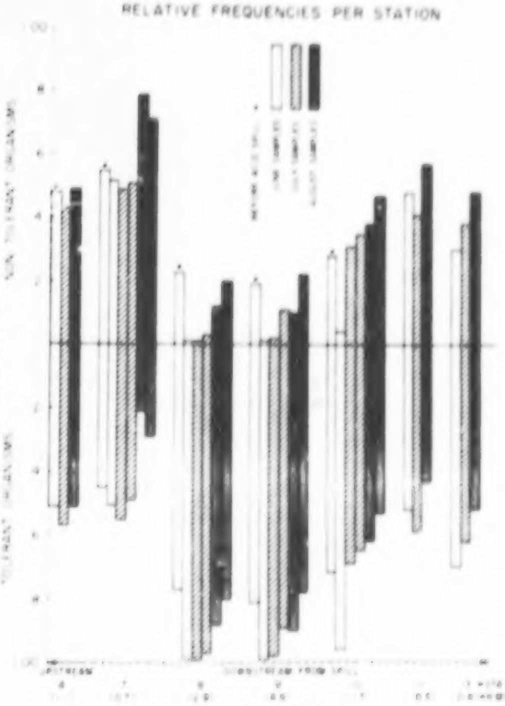

Figure 17. Relative Frequencies per Station for the June 19, 1970 Acid Spill.

elicit a response pattern in the macroinvertebrate and fish communities typified by an immediate reduction in the number of specimens. When no residual toxicity is found and there are undamaged areas available to act as sources for recolonizing organisms, a rapid recovery may be expected. Mill Creek had such a recovery when a small (100 foot) section of the creek was experimentally treated with acid immediately below an undamaged headwater area. By comparison, the biological recovery of the Clinch River from the acute pH stresses has been somewhat slower due to the severity and the extent of the biological damage.

A long term acute stress and stresses from materials with residual toxicities produce a similar but slightly different response pattern. Just as in short term acute stress situations, the general response pattern is an immediate reduction in both diversity (number of species) and density. However, with residual toxicities the macroinvertebrate organisms that survive the stress seem to be able to establish an interum type of community structure which lasts as long as the toxicity persists. For example, the Roanoke River had a residual toxicity from the ethyl benzene-creosote spill which was combined with a sedimentation problem and resulted in an atypical benthic community consisting of snails, midge larvae, mayflies, and stoneflies. This community did not have representatives from the caddis fly, riffle beetle, and crayfish families. The macroinvertebrate community found under continuous acid stress in the Indian Creek study was also atypical, consisting primarily of caddis flies and hellgrammites.

The rate of recolonization of damaged areas seems to be dependent upon 1) the distance an area is located from the site of the original spill and 2) the existence of undamaged tributaries. Those areas immediately below the site of the Clinch River spills were the first to show recovery. Reaches of the river further downstream were slower to recover. The rate of recovery is also faster below healthy tributaries as shown in the Indian Creek study.

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BIOLOGICAL EFFECTS OF SHORT-TERM EXPOSURES TO HAZARDOUS MATERIALS

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Environmental Protection Agency

In the course of this presentation an attempt is made to demonstrate that even short-term exposures to pollutants may lead to the impairment of species to survive, even though individual specimens may survive. Survival of the species is naturally taken to have greater ecological significance than survival of one or even a number of individuals. In many instances the so-called "fish kills" have great public impact, and yet a fish kill by itself may not necessarily eliminate a species from an area.

The damage of some pollutants which allow individual organisms to survive while preventing them from reproducing is far more insidious in consequence. These pollutants may literally annihilate a species or a whole segment of the biota by inhibiting the proper development or reproduction of key organisms within an ecosystem. To evaluate the probable consequences of likely environmental pollutants, a program of toxicological evaluations was developed for estuarine and marine macroinvertebrates and fishes.

A very important preliminary test in most toxicological programs on aquatic organisms is the 96-hr TL-50 test. During this short-term exposure, groups of organisms are exposed to a single pollutant at specific concentrations and under environmental conditions identical to those to which a group of controls are exposed. By this short gross evaluation of toxicity it is possible to derive the concentration of the pollutant which will kill half the animals tested within 96-hr. It is important to note that the TL-50 value obtained, which is expressed as a concentration, applies only for the species, the life stage and the environmental conditions tested.

The 96-hr TL-50 is a valuable tool in the establishment of ranges of toxicity for a particular compound or pollutant to a particular organism at a particular life stage and under restricted environmental conditions. With the same restrictions, the test can also be useful in pointing at probable antagonistic or synergistic effects of two or more pollutants. In addition, the 96-hr TL-50 can furnish information on the comparative toxicity of several toxicants tested separately under the same conditions.

According to the experimental conditions used at the National Marine Water Quality Laboratory (LaRoche *et al.* 1970), the 96-hr TL-50 for cadmium is approximately 80 mg/liter of Cd^{2+} as $CdCl_2 \cdot 2\,1/2\,H_2O$ when *Fundulus heteroclitus* (killifish or mummichog) is the exposed species. For this fish, copper and zinc alone have 96-hr TL-50 values which are 20 mg/liter for Cu^{2+} and 60 mg/liter for $AnCl_2$. These values must be further qualified by stating that they represent the initial addition of the elements to the seawater, since the solubility of copper, for instance, will decrease significantly within minutes of its addition to the exposure medium. Within one hour, the copper ion concentration in seawater will have decreased to 83% of the original concentration; by 8 hours only 5% of the original copper ions will be in solution and by 24 hours there is only 0.2% of the copper left in solution. Nevertheless, since copper will behave in a similar manner under identical conditions, the initial concentration added will be the value reported as a TL-50 concentration. Similar decrease in solubility could not be observed for cadmium or zinc.

With these 96-hr TL-50 values in mind and the solubility restrictions for copper, it should be added that these short-term exposures are carried out at 20°C in a synthetic seawater of salinity 20‰ and an initial pH of 8.0 (*Zaroogian et al.* 1969).

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Under the above conditions, the relative toxicity of varying combinations of Cd, Zn and Cu is summarized in Figure 1. Each delineated area represents a combination of added elements. For instance the first area on the left includes the results obtained with 60 mg/liter of Zn^{2+}, 0 mg/liter of Cu^{2+} and three concentrations of added Cd^{2+}: 0, 1 and 10 mg/liter respectively as shown by +0, +1 and +10 below the bars with a line across indicating the average of several values. Against the abscissa, the various ratios represent the concentrations of Zn^{2+} over Cu^{2+} in mg/liter while the ordinate represents the percent mortality within 96-hr of exposure.

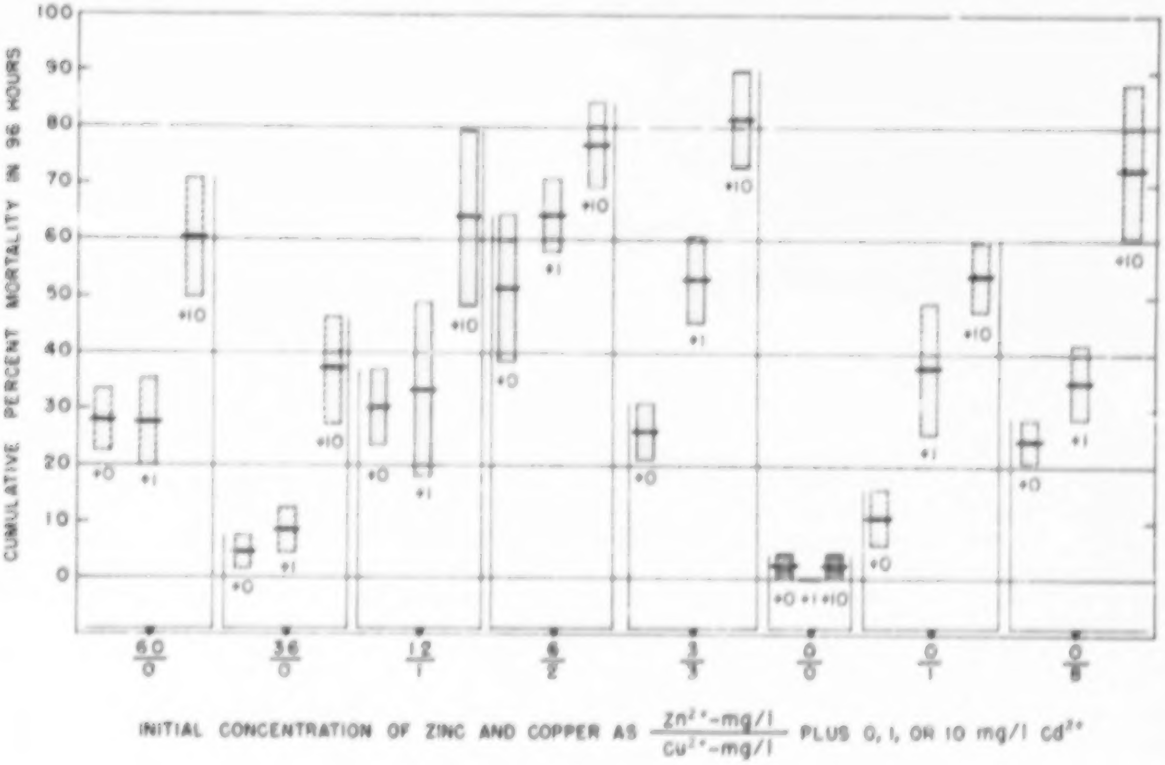

Figure 1

Examination of the sixth delineated area or column shows that at 0 mg/liter of Zn^{2+} and 0 mg/liter of Cu^{2+}, the addition of 0, 1 or even 10 mg/liter of Cd^{2+} does not cause a significant number of deaths within 96-hr exposures. It must be recalled that the 96-hr TL-50 for Zn^{2+} alone is 60 mg/liter for *Fundulus* and that this value for Cu^{2+} alone is 20 mg/liter. In addition, the 96-hr TL-50 for Cd^{2+} alone has been established at approximately 80 mg/liter for this species. Examination of the seventh column where fish are exposed to 0 mg of Zn^{2+} and 1 mg/liter of Cu^{2+}, in combinations with 0, 1 or 10 mg/liter of Cd, shows that there is a detectable degree of synergism in the toxicity of these elements within 96 hours. In the eighth column, the compounding effects of 10 mg/liter of Cd^{++} plus 8 ng/liter of Cu^{++} are evident. Synergism was observed at 3 mg/liter of Zn plus 3 mg/liter of Cu and the addition of 1 or 10 mg/liter of Cd^{2+} to these Zn-Cu mixtures produced more-than-additive toxicity. From this graph it is also noticeable that without Cd (*i.e.* Figure 1 +0 under the bars) 60 mg/liter of Zn (first column) appears as toxic as 12 mg/liter of Zn plus 1 mg/liter of Cu. In addition, these amounts are as toxic as 3 mg/liter of Zn plus 3 mg/liter of Cu or 8 mg/liter of Cu alone. A number of other semi-quantitative toxic similarities can also be observed in this graph which represents only a portion of the various combinations of these three elements tested on *Fundulus*.

As can be noted the 96-hr TL-50 is a valuable test which can be useful in the evaluation of relative toxicity of pollutants and in the establishment of probable additive or synergistic effects between pollutants. Also the 96-hr TL-50 is essential as a test to estimate the order of magnitude at which a chronic exposure test should be made. It should not be the sole basis from which criteria or even an application factor is established.

Figure 2 is meant to illustrate an important shortcoming of the TL-50 in that it does not take into

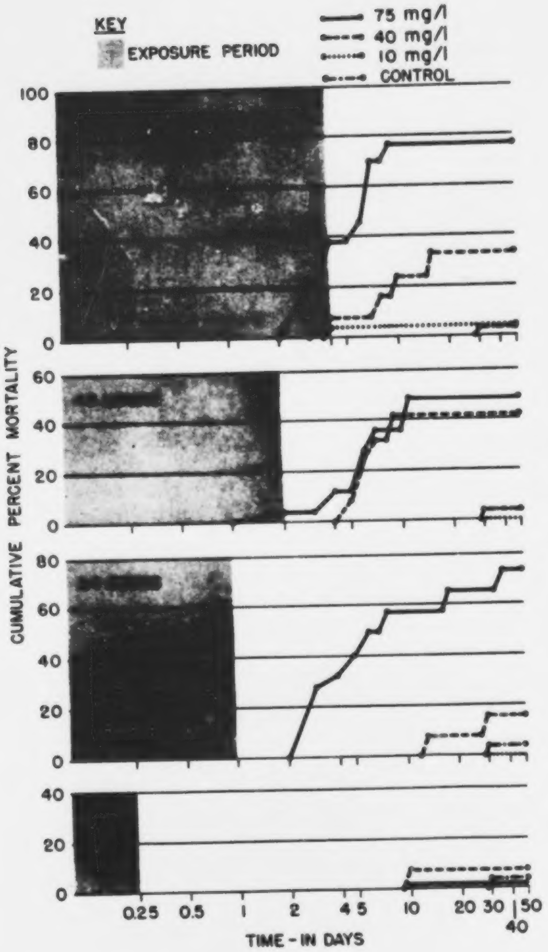

Figure 2

account the deaths of organisms beyond the period of exposure. The multiple graphs represent in this instance various exposure periods (shaded areas) followed by time periods where the fish were maintained in uncontaminated for a total of 50 days. The upper graph shows the results obtained if the fish are exposed to various concentrations of $CdCl_2$ for 96 hr (shaded area) followed by a transfer to uncontaminated water and maintained until the 50th day. It is clearly visible that a few days after the end of exposure a significant amount of intoxicated organisms have died.

The second series of graphs from the top show the survival after 48-hour exposures, while the two others show the survival of fish exposed to the same doses for periods of 24 and 6 hours respectively. Besides indicating the difficulties in obtaining chemically reproducible measurements with bioassays, this study demonstrates that *Fundulus* exposed to 75 mg/liter of Cd as $CdCl_2 \cdot 2\ 1/2H_2O$ for 24 hours were just as impaired in their 50-day survival as animals which had been exposed to the same concentration for 96-hours. In spite of the profound quantitative limitations attached to the 96-hr TL-50 it is still possible to derive valuable information which may guide efforts in the elaboration of biochemical, physiological or toxicological mechanisms associated with certain types of exposures.

Fundulus heteroclitus is recognized by most biologists as a most hearty fish. Most biologists would indeed be tempted to state that if it kills *Fundulus* it will most likely kill everything else. A concentration high enough to kill half the *Fundulus* during 96-hr exposure might be quite enough to annihilate many other more sensitive coastal species such as the bay scallop (*Aquipectens irradians*) or the silverside (*Menidia menidia*). This would be particularly true if one considers the latent toxicity of a pollutant such as Cd on *Fundulus* which will kill within 50 days more than 50% of the fish exposed to 75 mg/liter of $CdCl_2$ for only 24 hrs. (Figure 2).

As may be recalled the 96-hr TL-50 of *Fundulus* is approximately 20 mg/liter initial concentration for $CuCl_2$. It should also be recalled that within 8 hours only 5% of the initial concentration will be in solution and presumably available to the fish. In spite of this, *Fundulus* exposed to as little as 0.5 mg/liter of $CuCl_2$ showed significant histological damage within 24 hours after exposure.

Figure 3 shows a portion of a sensory center, within the cephalic extension of the lateral line in a control mummichog. This morphological appearance is indistinguishable from a similar specimen taken from nature. Note that the squamous epithelium lining the lumen of the lateral line canal appears relatively healthy. In addition, the sensory unit which includes sensory cells (neuromasts) and supporting cells appears unaffected.

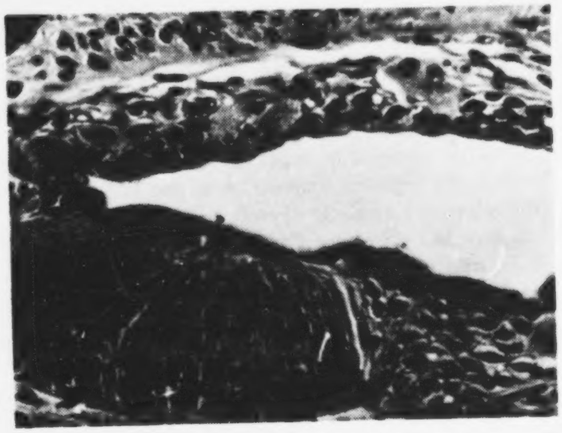

Figure 3

Figure 4 represents the effects of 0.5 mg/l of Cu^{2+} as $CuCl_2$ on the above structure only 24 hours after exposure. It is clear that the squamous epithelium lining the lumen is distinctly necrotic and contains pyknotic nuclei. Further, the germinating layers of this epithelium are also quite vacuolated suggesting that, even in the absence of a lethal dose, deep cellular changes can be noted. In addition to the damage on the squamous epithelium the sensory unit of this area is also severally afflicted. Note that there are few, if any, normal-appearing neuromast nuclei (sensory cells). It is evident that the deeper layer of supporting cells has also been afflicted by 0.5 mg/l of Cu^{2+} within 24 hours. Mostly pyknotic nuclei can be noted in the area.

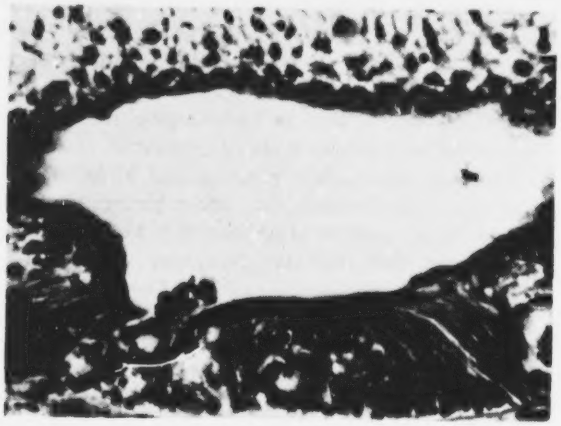

Figure 4

In order to ascertain the probable route of the corrosive action of Cu^{++}, experiments were set to test the effects of $CuCl_2$ injection. Volumes of 0.1 ml at levels as high as 50 mg/liter Cu^{2+} as $CuCl_2$ injected intraperitoneally daily for five days failed to show any sign of sensory cell damage within the cephalic extensions of the lateral line or the olfactory sacs. It therefore seems plausible to suggest that effects of $CuCl_2$ are from external contacts and that Cu^{++} incorporation does not have to be invoked to explain these pathological conditions. Under these conditions, it was also observed that the epithelium of the olfactory sacs showed visual degeneration which would definitely result in impaired olfactory responses. We have not yet extended our studies on the probable behavioral anomalies related to these findings, but it would appear quite reasonable to suggest that this damage would significantly impair the response of these fish to olfactory stimuli.

Figure 5 shows on one side of the lumen a series of well-differentiated olfactory chemoreceptors in the mummichog (killifish) (*Fundulus heteroclitus*). The receptor sites appear as healthy fibrillar pockets surrounded by supporting epithelial cells. The basilar area is densely nucleated.

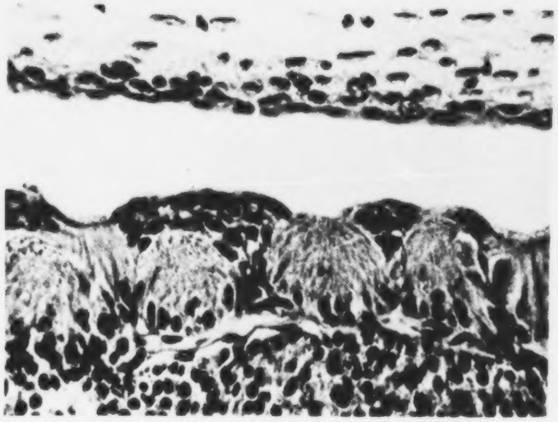

Figure 5

In *Fundulus* exposed to as little as 0.5 mg/liter of $CuCl_2$ for one day it can be noted that a very dramatic hyperplasia of the supporting epithelium has invaded the luminar space and has encompassed the olfactory sites. (Figure 6) A number of necrotic nuclei can already be observed within the basilar elements, the olfactory cells and the supporting epithelial cells.

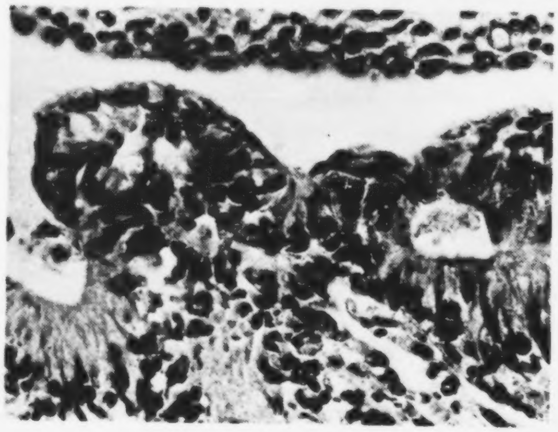

Figure 6

Figure 7 represents a similar area in a *Fundulus* which has been exposed to an initial concentration of 0.5 mg/liter of $CuCl_2$ for twenty-one days. It is clear that additional days at a low copper concentration show further damage where the chemoreceptor sites can be observed primarily because of their capsulated spherical shapes.

Figure 8 represents an olfactory area of a silverside (*Menidia menidia*) control. The chemoreceptor lamellae border of the flattened lumen is surrounded by numerous receptor sites. Note that the receptor sites are well-organized in rather symmetrical pat-

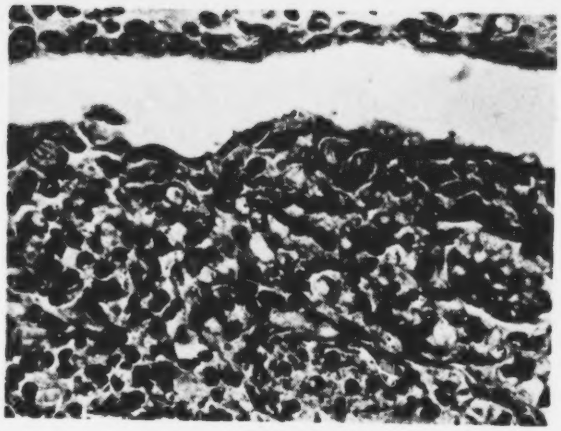

Figure 7

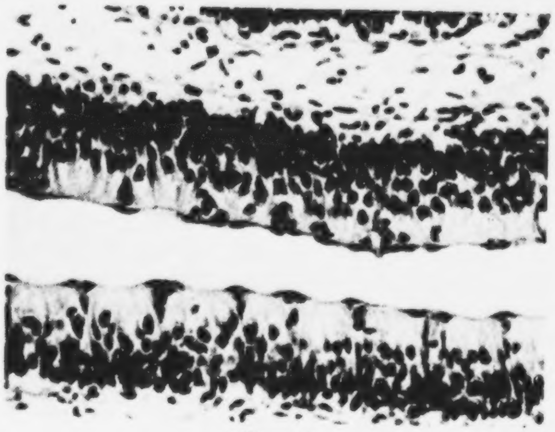

Figure 8

terns separated at the lumen by what appears to be a monolayer reticular cell arrangement. At or around each edge of the receptor site secretory cells are occasionally visible. The sensory site and accompanying supporting cells and basal cells are clearly stratified. Below the basal cells a submucosa formed of loose connective tissue is interspersed with few small capillaries.

Figure 9 shows the same area in a silverside that had been exposed to an initial concentration of 0.5 mg/liter of $CuCl_2$ for 6 hours. At this time, it is already evident that the entire architecture of the olfactory area has been completely destroyed. The vestiges of a few badly cantorized chemoreceptor sites are barely visible. The lumen has been shrunk into an irregular shape by an obvious swelling of the submucosa where a distinct hyperhernia can be identified through increased vascularization. The basal area of each chemoreceptor site is also destroyed and necrotized.

At 0.5 mg of Cu^{++} /liter it is clear that the damage caused is overwhelming since few, if any, of the fish exposed would have survived. It is then expected that much lower doses over extended periods of time could be far more insidious in that they might cause similar injury, inhibit olfactory responses and thus prevent the survival of species.

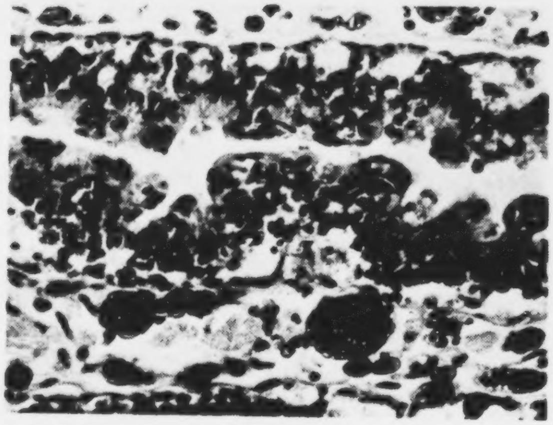

Figure 9

On March 16, 1971, a No. 2 fuel oil spill was detected in Long Cove, Searsport, Maine. The seepage made its way into a drainage system which emptied out through a 3-foot pipe into Long Cove. The oil spill of unknown gallonage covered 124 acres and was reported to have killed approximately 8800 bushels of softshell clams (*Mya arenaria*). Approximately four months later surviving clams from the area were submitted to a systematic histological examination, along with control clams taken from an area five miles away which had not been affected by a spill. The incidence of gonadal tumors in clams clearly increased when taken near the source of the spill as over one quarter of the clams demonstrated typical lesions.

Figure 10 represents the low power magnification of a section through the testicular chords (follicles) of the gonad in the intact softshell clam (*Mya*

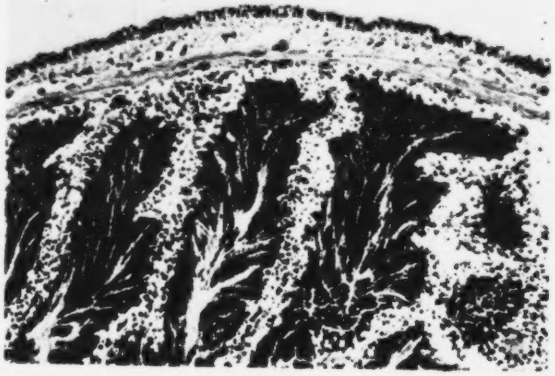

Figure 10

arenaria) from a control area. Notice the top, the outer wall (serosal surface) of the shell-fish. This serosal surface comprises a tall epithelium interspersed with secretory cells. Against the epithelium a connective tissue layer precedes a thin muscle layer which appears to engulf the testicular entity where the darker more densely nucleated spermatozoa appear as dark radiating alveoli fitted within loose connective tissue septa.

Figure 11 represents a condition observed in a softshell clam obtained from the site near the origin of the coastal No. 2 fuel oil spill. The same peripheral anatomy as in the control can be noted; however, in this instance the testicular tissue has been transformed into aggregates of nucleated cells devoid of the appearance observed in controls. The typical architecture noted in the control is no longer present except for the compressed aspects of loose connective tissue septa. The virtual absence of spermatozoa and the extensive development of spermatogonial elements characterized this germ cell tumor as relatively malignant.

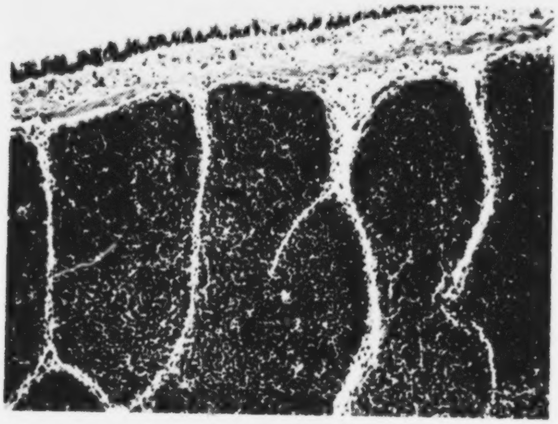
Figure 11

Figure 12 shows an affected area of the gill in a softshell clam where a germ-cell tumor has been identified. In this section a relatively unaffected portion of the gill filaments can be observed on the right. Above the water tube the much darker densely nucleated mass appears to invade the outer gill lamellae. This hyperchromatic development is definitely hyperplastic and could conceivably represent a secondary tumor of germ cell origin that can be defined as a metastatic lesion. In this event it would appear plausible to suggest that these profound changes present in surviving softshell clams from this oil spill area are reminescent of cancerous tissues observed in other species.

From these observations it is certainly tempting to conclude that No. 2 fuel oil has in the course of a few months increased the incidence of tumorous lesions. However, at best the current findings are informative and can be most valuable in the elaboration of an experimental protocol capable of demonstrating, under controlled conditions, that fuel oil No. 2 is the principle causative agent of lesions.

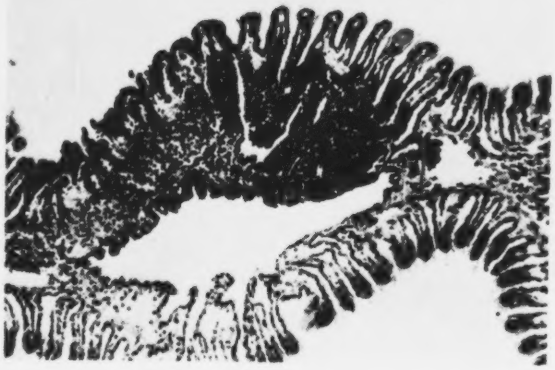
Figure 12

It is a fact, that approximately four months after the oil spill in question, surviving softshell clams nearest the source of the spill showed lesions. It is also a fact that one month later a broader area showed specimens which had developed lesions. However, the principal question at hand is still: can fuel oil No. 2 *alone* produce these lesions? There is very little doubt that the oil spill was the main agent killing 8800 bushels of clams within a few days of the incident. However, we cannot be certain that oil alone produced the tumorous lesions. Only a controlled experiment duplicating the spill conditions can clear this point; otherwise, a number of questions may still cast doubt on the implication. For instance: 1) is it oil alone that has produced the lesions? 2) is it one or several other pollutants in combination with the oil that are the causative agents? 3) can these lesions occur in the absence of No. 2 fuel oil? 4) how long does it take for the condition to develop? 5) can other pollutants stimulate the development of the lesions? In other words, fuel oil No. 2 appears to be implicated in the development of tumorous lesions in this shellfish; however, the identification of a polluting substance does not exclude the presence of yet unidentified damaging substances which could have by themselves induced the morphological disorders. As can be noted, this very interesting partially-monitored ecological and histopathological observation furnishes an insight into what needs to be confirmed experimentally.

So far this presentation has dealt with damage that may occur in species from the coastal or marine environment. At this point it might be profitable to discuss the probable public health hazards related to an elemental pollution which might be likely to accumulate in edible species.

The World Health Organization has stated as recently as 1963 that cadmium in drinking water at concentrations above 10 micrograms per liter may be a hazard to human health.

An experiment was initiated to establish the probable effects of 10 micrograms/liter of added $CdCl_2 \cdot 2\ 1/2\ H_2O$ in flowing coastal waters to adult killifish (*Fundulus heteroclitus*), lobster (*Homarus americanus*), scallop (*Aquipecten irradians*) and oyster (*Crassostrea virginica*). The exposure time lasted 21 days during which time there were no differences in the mortality rates between exposed organisms and controls. At the end of this experiment a number of organisms were examined for preliminary histopathological evaluations. In addition, cadmium contents were made by atomic absorption spectroscopy to estimate the probable accumulation associated with exposure.

The results revealed that there were no distinguishable histological changes between exposed organisms and controls. Systematic histological comparison could not reveal any visible differences in the tissues of the exposed organisms when compared with their respective controls. Cadmium determinations in the various exposed species and controls revealed that a significant concentration of cadmium was noticeable in some exposed species as opposed to the controls (Table 1).

TABLE 1

Cadmium in whole body and selected tissues of four marine species after immersion for 21 days in flowing seawater containing 10 micrograms/1 of cadmium (as $CdCl_2 \cdot 2\ 1/2\ H_2O$).

Species	mg Cd/kg ash wt		mg Cd/kg wet wt	
	Exper.	Control	Exper.	Control
Fundulus heteroclitus				
whole fish	7.6	5.6	0.48	0.33
Homarus americanus				
whole lobster	5.4	5.3	0.72	0.51
exoskeleton	4.4	4.1	0.88	0.59
gill	31.3	17.2	0.87	0.49
viscera	37.5	33.8	1.21	1.21
muscle	11.7	10.0	0.25	0.20
Aquipecten irradians				
whole scallop	82.7	34.0	2.46	1.15
adductor muscle	74.1	49.2	1.68	1.41
remainder	85.0	29.5	2.74	1.05
Crassostrea virginica				
whole oyster	52.1	9.3	1.49	0.33

As can be noted, edible portions of exposed lobster (muscle), scallop (abductor muscle) and oyster (whole animal) contained more cadmium per unit wet weight than controls by 25%, 19% and 412% respectively (Table 1). It should be suggested that if this elemental concentrating scheme exhibited by the oyster proceeds at the same rate beyond 21 days, this species should become a hazard to human health if eaten.

CONCLUSIONS

1. Short-term bioassays (including the 96-hour TL-50) and field observations can offer valuable assistance in the identification of toxicological responses. The short-term assays are also most valuable in the establishment of realistic chronic exposure studies. However, bottle tests should no longer be satisfactory to obtain ultimate indices of toxicity. Bioassays should more nearly reflect realistic conditions of environmental exposure.

2. Inherent synergisms between heavy metals and between other pollutants and environmental conditions *prescribe* the necessity to initially screen pollutants under specific and well-controlled conditions.

3. Subtle damage, as it may impair the survival of a species, should be sought and identified by pursuing all plausible methods of sensitive bioanalysis. Thus, when a pollutant concentration has been related to the damage, a basis has been established for the development of a so-called application factor.

At this point a criteria for biological systems is then available and standards for a particular area may be set.

4. The establishment of standards for marine or coastal water must not ignore the affinity of edible species to concentrate pollutants to a point where they may become public health hazards without showing any degree of impairment themselves.

5. Monitoring the environment will not necessarily furnish anything more than recorded evidence of a catastrophy, unless well-controlled experimentation has shown what we should be monitoring and for how much. Therefore it is not until standards have been established with some degree of realism that monitoring and enforcement can have a serious role to play in the control of pollution.

ACKNOWLEDGEMENTS

All the experimental work presented herein has been developed by the following workers (in alphabetical order): Marcia Barry, Ronald Eisler, George Gardner, R. Hennekey, Eugene Jackim, Paul Yevich and Gerald Zaroogian of the National Marine Water Quality Laboratory. The assistance of Nelson Thayer, Shirley Wilkins and Denise McNulty is gratefully acknowledged.

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ACUTE AND CHRONIC TOXICITY ASPECTS OF CHEMICAL SPILLS

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The choice of Houston as a location for this National Conference on Control of Hazardous Material Spills is quite appropriate, and the planning committee is to be congratulated. Houston not only has its University with the well-established concerns and action program for clean water; Houston also has the Manned Spacecraft Center which provides us with an opportunity for a different perspective on our water pollution problems. Throughout this Conference was have been taking an almost microscopic look at water, and it may be worthwhile to step back for the larger view.

Everyone will recall that beautiful classic picture of the Earth from outer space. There is our little ball with its fleecy white cloud cover and its large expanses of blue water. There are a few brown areas of land. Dr. Walton Smith, Dean of the Rosenstiel School of Marine and Atmospheric Science, at Miami, described the impact this view would have upon a scientist from another plant.[1] The visitor would recognize that water dominates this planet and that its unique physical chemical properties make all these myriads of forms of life possible. It not only controls our climate but it controls the very structure of our genes by hydrogen bond formation. Water merits our highest respect and greatest concern.

Consider the four compounds in Table I. These are commonly looked upon as environmental pollutants presenting significant threats to the health of most life forms. The dates in that Table are the years in which these compounds were discovered in interstellar space. According to many cosmologists these were involved in the very beginnings of life as we know it. Are these compounds life-threatening or life-giving? The answer, of course, is that they are both and the differentiation involves concentration. That is what toxicology is all about—how much is too much and how much is safe. The fundamental precept of toxicology states that all materials are toxic at some dose level and by some route of administration. A corollary states that all materials are safe at some dose level and by some route of administration. These concepts hold true for water and oxygen and for those compounds in Table I and all other materials.

Let us examine how this precept and a few other principles of toxicology can assist the pollution control officials with problems arising from spills of hazardous chemicals. Toxicology can give the official two basic pieces of information. It can describe the kind of injury that may be expected from a material, and it can provide quantitative information about the anticipated severity or extent of injury. These pieces of information are important to the control official for both planning preventive action before a spill and prescribing corrective action after one occurs.

Spills are accidents. They are single events occurring in a restricted section of the environment. They are not likely to be repeated in any given place although they may happen again somewhere else. They are unpredictable as to time or place. In order to prevent spills in a realistic manner and to cope with those that do occur, the control official must have adequate toxicity information in advance of a possible spill.

TABLE I

Ammonia	1969
Formaldehyde	1970
Hydrogen Cyanide	1970
Carbon Monoxide	1971

Ideally, complete toxicity information should be available on all chemicals that might be spilled. This should include the effects on all target organisms by all routes of exposure (contact, ingestion, and even inhalation). The collection of truly complete toxicity data on a single chemical is probably an impossible and never-ending task. Certainly, it constitutes a major effort involving the commitment of large amounts of time, money, technical skills and facilities. Compromises must be made between the ideal and the practical.

Fortunately, toxicology does not force us to make all of these compromises and decisions at once. In practice toxicology is a sequential science; it proceeds in small steps and small decisions are made at each step. It begins by determining the effects of a single compound on a single species, by a single route of administration. This is usually done by giving rats a series of single oral doses of increasing size. The resulting data produce a graph looking like Figure 1.

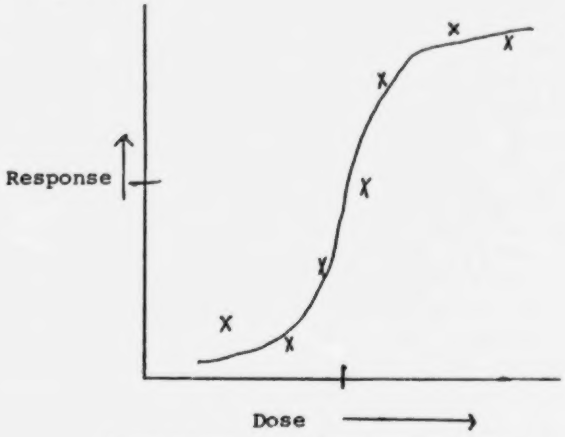

Figure 1: Acute Toxicity Dose-Response Curve

It is most intriguing that the same shape of graph results (a) regardless of the species used—rats, dogs, fish, birds, or man; (b) regardless of the response observed—death, irritation, nausea, convulsions, or mental acuity; (c) regardless of the route of administration—oral, skin, inhalation, or intravenous injection. The numerical values will, of course, differ between species, routes, and responses and the slope of the curve will vary.

Such graphs can be compared with each other by means of the dose that is related to the response of 50% of the maximum. If the response observed is death, then this point is the familiar LD_{50}, the dose which is lethal to 50% of the test organisms. It is important to remember that the LD_{50} is not an absolute value. It is a statistically derived approximation. As Figure 1 shows, the data are always scattered. We believe this is due to the inherent variability of living systems—no two are exactly alike even if they are highly inbred.

These kinds of single exposure, acute toxicity data are commonly used as the basis for regulation of materials being transported.[3,4] There is good justification for this. Acute toxicity data are quick and relatively inexpensive to obtain. There have been many thousands of such determinations made in the past fifty years, so the toxicologist can make a good preliminary estimate of the relative toxicity of a material from its acute toxicity. However, the control official is confronted with two problems in applying acute toxicity data to controlling a spill of some hazardous material.

First, an LD_{50} and the rest of the acute data are only measures of toxicity; they are *not* a measure of hazard. Toxicity data can give you a good idea of what will happen when a certain dose is delivered to an organism. Hazard involves the probability of that dose ever being delivered. Hazard determination is the main concern of the control official. He must evaluate the total circumstances of the spill. Other properties such as solubility, volatility, reactivity must be taken into account in judging whether a given spill presents an environmental hazard because of its toxicity. An excellent proposal for a comprehensive hazard evaluation has been made.[5] Any spill hazard evaluation system must also take into account that the spilled material is in addition to whatever other contaminants are already present. Many of the concepts and concerns voiced by the Committee on Toxicology regarding short-term air pollutants are applicable to water spills.[6]

The second problem the control official has when using acute toxicity information is in deciding if single dose data are applicable to the real or expected spill conditions. For example, visualize a persistent material spilled into a small lake or slow flowing stream. The wild animal coming to the shore for a drink essentially gets a single dose, but the fish and other aquatic life get a continuous long-term or chronic dose. If the control official is concerned about fish he needs a lot more than a rat oral LD_{50}. He needs data from chronic exposures of fish and their food organisms.

Pursuing this example a step further, if the control official believes, as I do, that his primary responsibility is to protect human health and secondarily, but importantly, to protect fish and wildlife, then what kind of toxicity data does he need when this body of water is the raw supply for a community?

Obviously, for short-lived substances the control official will think first of simply shutting off that water source so that people have no exposure. If the contamination is going to persist long enough to deplete stored water supplies the control official needs to know what concentration is safe in drinking water. Establishing such a standard requires expert judgement of the highest caliber, and it will be based upon long-term feeding studies in a variety of species at dose levels bracketing the anticipated concentration. The toxicologists conducting and evaluating these studies will be looking for evidence of accumulation of the compound up to dangerous levels in some body tissues. They will be watching for signs of delayed effects. They and the control officials will be concerned about whether there are people particularly susceptible to the compound.

It seems clear that the control of hazardous material spills requires a large volume of toxicity information for both prevention and correction. A system should be established to collect the necessary toxicity data and to obtain professional evaluation and recommendation in advance of spills. In developing standards under such a system the seven commandments proposed by Dr. Stokinger[7] should be observed. They are shown in Table II.

TABLE II

Seven Commandments for Environmental Health Standards[7]

1. Must be based on scientific facts.
2. Must be completely documented.
3. Avoid unnecessary severity.
4. Determine realistic levels.
5. Use scientific judgement on carcinogenticity data.
6. Determine trends, not pro tempore monitoring.
7. Delimit banning.

The control official has one further cause for concern involving toxicology. It has become common practice in the event of spills for housewives, boy scouts, and other volunteers to proceed immediately to the rescue of the local flora and fauna and to shovel up the mess. The control official has a responsibility to be sure that these commendable efforts and intentions do not result in some form of poisoning of these citizens. An important step in this direction is the labelling and placarding system recently developed by the Manufacturing Chemists Association.[8]

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HAZARDOUS MATERIAL SPILLS vs OIL SPILLS COMMON BIOLOGICAL DENOMINATOR?

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ABSTRACT

Factors influencing the type and intensity of adverse biological alteration resulting from hazardous material and oil spills are demonstrated using "on-scene" color slides. Spill control and treatment methodology, which potentially may be more detrimental to the ecology than the spilled material itself, are discussed.

Potential routes of injection, contamination and subsequent alteration by the indigenous population are outlined. Anticipated effects from hazardous material spills on estuarine plankton, mudflat, and rocky shore communties, plus a fresh water lotic environment, are postulated based on documented ecological alterations observed from past oil spills.

It is recognized that spills of oil or hazardous materials affect the total environment—terrestrial, air, water—and that immediate response is essential from all medias to control, monitor, and cleanup the incident. The Environmental Protection Agency, through its National Environmental Research Centers (NERC), is attacking this total problem; however, for the purpose of this paper, only the "water phase" will be discussed, as this is the area of research responsibility assigned to the Edison Water Quality Research Division of NERC, Cincinnati.

Is there a common denominator between oil spills and hazardous material spills? When comparing visibility, namely oiled beaches and oil coated ducks, obviously there is not; however, when we compare the many properties of oils and hazardous materials, (toxicity, solubility, biodegradability, volatility, density and surface activity) that may influence their effect on the environment, unquestionably there is a relationship. In addition, biological damage caused by such spills, whether they be associated with oil or hazardous materials, will be governed by a combination of factors, including, but not necessarily limited to:

- *(a) Type, quantity, and composition of material spilled;*
- *(b) Duration and persistence of the spill;*
- *(c) Hydrography of the area;*
- *(d) Treatment and/or control methods used to clean up the spill;*
- *(e) Climatic and seasonal changes;*
- *(f) Indigenous biota.*

Type, Quantity, Composition of Spill Materials

The most serious biological effects resulting from any type of spill incident—oil or hazardous materials —are a direct function of the type and quantities of materials spilled. Like oil, the chemical composition of the hazardous materials will dictate the acute as well as the sublethal responses of the eco system. Damage to the environment may take the form of

Type, Quantity, Composition of Spill Materials

The most serious biological effects resulting from any type of spill incident—oil or hazardous materials —are a direct function of the type and quantities of materials spilled. Like oil, the chemical composition of the hazardous materials will dictate the acute as well as the sublethal responses of the ecosystem. Damage to the environment may take the form of causing a) destruction of the food resources; b) destruction of the more sensitive juvenile forms of organisms; c) direct death through contact or exposure, coating, and asphyxiation, or d) incorporation of sublethal amounts of the spilled material into the organisms, resulting in reduced resistance to infection and stresses.[1]

Unlike spills of oil, where the major water quality parameters considered are aesthetic effects and aquatic and plant toxicity, spills of hazardous materials must also include human toxicity. This critical human concentration, which can be defined as the maximum allowable level for domestic water supplies, must constantly be monitored if substantial damage is to be prevented. Information concerning the public health hazard is especially critical when determining the extent of and how rapidly a biological sampling program, designed to assess damage, can be initiated. In some instances, the spill area may have to be cordoned off until detoxification takes place prior to initiating biological investigations.

Biological damage resulting from an incident is not necessarily keyed to simply the volume of the spilled material, but rather to the concentration of chemical in the affected area. In oil pollution, an example of this would be the West Falmouth incident.[2] By volume it was only 1/100th the size of the Torrey Canyon incident and yet the biological damage resulting from this spill was almost catastrophic.

Duration and Persistence of the Spill

Duration and persistence of a spill is dependent upon the specific physical and chemical properties of the spilled material itself, as well as on the chemistry of the receiving water and the type and degree of benthic deposits and aquatic life. Impairment to water quality may be persistent in nature when the oil and/or contaminant becomes attached to or absorbed upon various organic materials within the water. For instance, oil may become absorbed onto suspended particulate material allowing it to remain in the environment for a longer period of time: or, it may undergo degradation or alteration in nature, thus influencing this detrimental effect. In this same manner, the biological accumulation and magnification of the persistent compounds remaining after weathering or alteration by microbial action may be present when oil is absorbed onto the detritus, which may be used by filter-feeding organisms as a food source. The hydrocarbons incorporated into the filter feeders may be passed onto the next level of consumption gradually, the concentration in the various organisms involved in the food web is increased.[3]

Hydrography

Knowledge of the physical and chemical behavior of a spill substance is of utmost importance if damage is to be minimized, control and recovery measures instituted, and proper notification steps initiated. Physical features of the receiving waters, including currents, tidal exchanges, coastal patterns and wave action, are extremely important and affect the distribution and time of exposure of the organisms to the spilled material. The relative hazard of an unseen spill, specifically of hazardous materials, is inherently greater than that of readily observable oil spills.

Treatment Systems

Treatment methods used to control and clean up an incident can potentially cause more damage to the environment than the spill material itself. In cases of oil spills, indiscriminate use of dispersants would fall into this category. Studies[4,5] have demonstrated a greater effect in terms of environmental damage to the pelagic community when oil is forced into the water column through the use of such chemicals. When considering hazardous material spills, exchange, precipitation, biodegradation, and/or dispersion procedures will most likely be used to clean up the incident if physical containment or removal or both is impractical. The possible synergistic and/or antagonistic effects of these procedures are uncertain; however, it is highly probable that one of these procedures will increase the severity of the damage to the aquatic environment, especially when the environmental priority established at the scene of the spill is "man."

Battelle,[7] when assessing neutralization procedures for handling soluble hazardous material spills, concluded that this treatment method was potentially more damaging than the original contaminant.

Climatic and Seasonal Changes

The rate, extent, and direction of biological and/or microbial transformations will be dependent upon environmental conditions, namely pH, dissolved oxygen, temperature, nutrient, salinity, light, and the type and quantity of available energy. Thus, climatic and seasonal changes may significantly influence the effect of a spill on the environment because conditions in the receiving water may be rapidly altered. In cases where seasonal flooding may occur, coastal salinities would be lowered and as a result, sedentary species would be under stress prior to being exposed to any spill material. In addition, where agricultural runoff is of concern, increases in pesticide levels would most likely occur, possibly masking the effects of a spill incident. Straughan[6] inferred this was a problem during the Santa Barbara incident.

Indigenous Biota

Because of our preoccupation with the visible effects of spill incidents, little attention has been given until recently to the problems associated with the "unseen" soluble fractions of oil and/or hazardous materials. Recent scientific studies have identified the processes and mechanisms by which marine and aquatic organisms biologically modify and concentrate chemical materials through successive steps in the food chain. Thus, materials spilled into the water environment may initially be at concentrations considered to be inconsequential; however, a combination of biological and chemical physical processes can lead to concentrations at hazardous levels. Figure 1 illustrates these processes.[7] Pesticides, mercury and many other heavy metals are examples of this phenomena.

Predicting the Future?

This nation has yet to experience a hazardous material spill of a magnitude equal to a *Torrey Canyon* or *Ocean Eagle*. Past major incidents have been on a small scale, or water quality aspects have attracted little or no attention because of the fire, explosion, or air pollution threats. However, with predictions of more-frequent and higher-volume bulk shipments,[8] it is only a matter of time before we are faced with a major incident.

Thus, it is desirable to extrapolate our knowledge from the area of biological damage resulting from oil spills, to the problem of hazardous material spills.

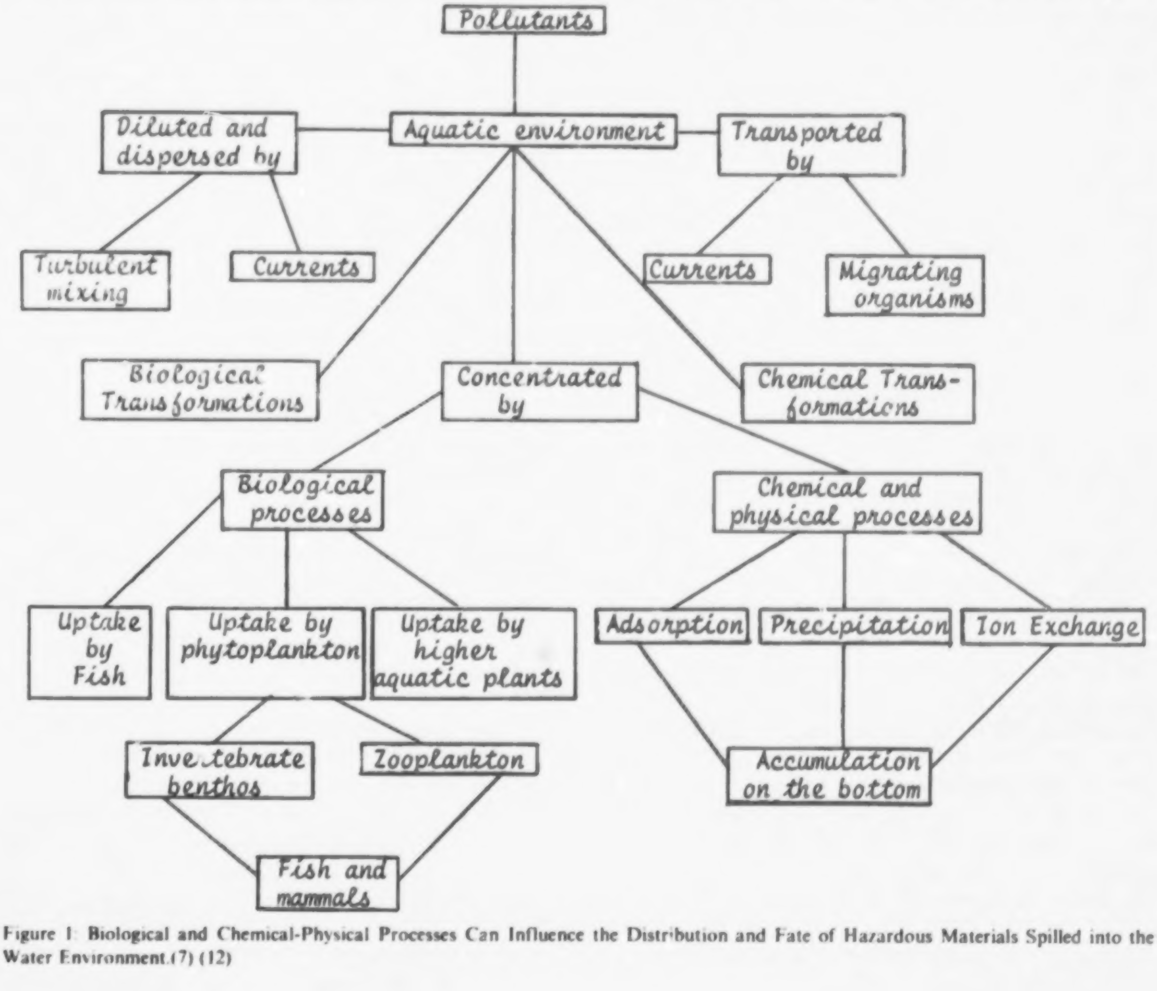

Figure 1: Biological and Chemical-Physical Processes Can Influence the Distribution and Fate of Hazardous Materials Spilled into the Water Environment.(7) (12)

Discussed will be three different ecosystems—coastal waters, intertidal areas, fresh water habitats—and how, based on our experience with oil, they may react to a hazardous material spill. From the Battelle study,[7] which gives a priority listing for hazardous materials, the assumption is made for this paper that oils are, by nature, less soluble than the most troublesome hazardous materials.

Coastal Environment Ecosystems

Estuarine Plankton Communities

In the past, most major oil spills have taken place in coastal waters. On the other hand, hazardous materials spills have primarily occurred in inland waters or in the terrestrial environment. However, with the advent of increased waterborne traffic and the development of supertankers for transport of hazardous materials, the threat of hazardous material spills to the coastal environment is increased. In this light, concern must then be given to the effect that these materials may have upon the aquatic communities of the coastal areas. For contrast between the effect of oil and the potential effect that hazardous materials may have upon these coastal ecosystems, let's examine the reaction of the contaminant to the communities involved.

As a general rule oil remains on the surface, with diffusion into the water column accomplished or intensified by the amount of turbulence, wind intensity, and tidal currents and also by the type of oil present. Acute effects may be seen over a large area as the oil is transported on the surface via wind and water movement. The surface plankton are apt to be affected first as the soluble components within the oil diffuse into the water column. Sublethal concentrations of the hydrocarbons may induce narcotic effects upon zooplankton, thus hampering the natural swimming movement and possibly impairing their capacity to escape predation.

Within the open water ecosystem, the solubility of hazardous materials is also extremely important in determining the type of effect that will be noticed. The diffusion rates of these materials, which generally are greater than those associated with oil, will cause these chemicals to be rapidly incorporated throughout the water column. Thus, it is likely that more acute biological effects will result.

Looking at the affected area as a singular water mass, negating currents and upwellings, the large dilution factor will usually influence the reaction of the plankton community to the spill material. The effect upon the indigenous organisms will be inversely related to the distance from the injection point.

Intertidal Environments—Rocky Shore

The coating action of oil is highly pronounced and noticeable within the upper intertidal reaches of the shore. Its significance depends on the type of oil and the thickness coating the rocks and organisms. Release of viable oil components into the water by the tide and wave action will likely affect the intertidal organisms. Narcosis and even death may occur as was evidenced following the *Torrey Canyon* when limpets were affected by the oil and the dispersants used to clean up the spill. Smothering the organisms occurs only when the oil adheres to the respiratory surfaces of the organisms, impairing gaseous exchange. Other than Santa Barbara,[10] few cases of actual smothering have been documented. It is more probable that the delicate respiratory tissue surfaces are damaged by the leaching of the toxic hydrocarbons from the oil.

Hazardous material spills that might involve or affect the intertidal rocky shore ecosystem involve conditions much different than that of oil spills. Unless a froth or flock has formed from materials reacting with the ionic constituents of seawater, smothering of intertidal populations is unlikely. With most hazardous materials spills, the populations will be exposed to a seawater mixture solution of the hazardous material. Toxic components within these solutions will induce narcotic and lethal effects particularly in the tidal pools where the organisms will be constantly exposed to the spill materials.

A potential detrimental effect to estuarine populations is alteration in the organisms' capacity to osmoregulate. This essentially means the ability of the organism to maintain its internal fluid concentrations within the cells of its body. After a spill occurs, collecting sluggish and dying organisms from the affected areas may help to denote the type of affliction; for instance, whether the material affected the respiration or osmotic regulation. Osmotic functioning is most important for estuarine populations. Most of these organisms have a total concentration of materials within their cells equivalent or nearly equivalent to the concentration in seawater. Their being able to live in an estuarine environment, which essentially is a mixture of seawater and fresh water, means that they have developed a capacity to maintain their internal concentration by excreting excess fresh water that seeps into their bodies. If they lose this capacity, the organisms will die.

In oil spills, water, sediment, and organisms are analyzed to determine background hydrocarbon levels and to estimate the degree of contamination from the most recent spill. Analysis of hydrocarbons in biological tissues is a problem because of the natural hydrocarbon content present in the organisms and the rapid alteration of any oil that might have been recently spilled. A similar sampling program to determine the effects of a hazardous material upon the aquatic organisms must be implemented. The analytical problem of detecting and identifying a hazardous material and/or its components is more difficult than that associated with the analysis of spilled oil because of the vast array of hazardous materials. In light of this, it may be some time before we are able to make definitive statements concerning the effect of a hazardous material spill upon the local ecology.

Mudflats — Intertidal Area

Mudflats are inhabited by a variety of different organisms. These include deposit, burrowing, and filter-feeding populations. Some are shelled creatures, e.g., clams; others are soft-bodied, e.g., polychaete worms, burrowing anemones, nemerteans.

From past spills involving mudflats, both shelled and soft-bodied creatures have been affected adversely. At the West Falmouth[9] spill, acute effects were noticed initially with mortality occurring with the adult populations on the mudflats and salt marshes. Later on, attempted resettlement of the mudflats by pelagic larvae immigrating into the area from adjacent uncontamnated mudflats was impaired by the large residue of oil remaining within the sediments. The sediments had absorbed some of the hydrocarbons and formed a hydrocarbon sink. A hazardous material spill could bring about a similar series of ecological events, especially if the spilled material was absorbed onto the sediment particles. Incorporation of these materials into the food webs associated with mudflat communities is entirely possible providing that lethal levels are not reached within the food web populations. Without any alteration or detoxification, biological magnification could occur and result in inordinate amounts of spilled material in the tissues of the scavenger and carnivorous populations.

Fresh Water Habitat

River or Stream Ecosystem

Inland oil spills primarily involve small streams and rivers that ultimately flow into a larger body of water. Oil discharged or drained into storm sewers will also gradually find its way into a feeder stream of a lake or river. This method of injection is more the rule than the exception. Hazardous materials enter the environment in the same manner, particularly when transportation accidents are involved. Projected estimates[8] reveal accidents involving railroad tank care are increasing 5.8% per annum. This rate increase is related to the increase in train velocity and carrier tonnage. Derailment and tank car rupture are the most common means of spillage involving fresh water biotic communities. The effects of such spills are frequently very dramatic since high concentrations of toxic materials purge the stream, wiping out whole population assemblages.

Fish kills are the most noticeable indicator of biological damage following a spill in the lotic habitat. The inference of a fish kill is that other populations are adversely affected as well. In most cases, this is probably true, but with oil spills, fish kills are not as prominent. Fish may avoid the contaminated area or have a higher degree of tolerance to the soluble components. Fish mortality usually occurs when the fish are exposed to shock loads or purging and have no way of escaping.

In most spills, certain species, particularly the surface feeders, will be affected, i.e., cladocerans, etc. The intensity of the kill and species involved is dependent upon the depth of the water in the stream and the degree of contaminant incorporated throughout the water column.

The same criteria used to judge the effects of oil and hazardous material spills on the pelagic estuarine ecosystem should be used here for the river or stream ecosystem. Spreading oil will affect the bank communities of emergent plants as it moves downstream. This community may be made up of a few cat tails or may be a complex freshwater marsh with multi-speciation and very high productivity within the stream drainage system. Therefore, it cannot be regarded as a minor community when looking for total effect.[11]

Waterfowl and aquatic mammals, e.g., muskrats, will be stressed differently by an oil spill than by a soluble hazardous material. Acute effects of an oil spill on these populations are loss of buoyancy and swimming capacity from oil emersion and toxicity from oil ingestion. A hazardous material potentially could cause narcrosis of the submerged portions of their bodies and damage to the respiratory tissues from inhalation of the fumes.

Soluble hazardous material spills will contaminate the entire water column and be rapidly dispersed downstream from the injection site. The effect on the emergent vegetation community as well as the benthos and submerged communities will depend upon the solubility, diffusion rate, and relative toxicity of the matierial. Contaminated organisms killed or narcotized by the hazardous material will be swept downstream to contaminate other water masses. This is a very real problem for, in some cases, biological tissue will absorb the toxicant material from the water and result in a higher concentration in the tissue than in the water itself. These materials, if not altered by microbial or physical interaction with the aquatic environment, can potentially affect a new area.

SUMMARY

Materials classified as hazardous are more diverse in chemical nature and behavior when released in the aquatic environment than is petroleum. It is dangerous to attempt a generalization concerning interaction and effects of these materials upon the various biotic habitats, especially when we know so little concerning the reaction of biological communities to these materials. However, a few statements can be made:

a) Oil with its floating nature will spread quickly over the water surface and contaminate the intertidal zones of the estuary. Under tumultuous conditions, it will also affect the entire water column and benthic community. Soluble hazardous materials will affect all of the aquatic communities; it will diffuse, disperse, and be diluted to a much greater extent than oil. Potentially, depending upon the material spilled, the natural ionic constituents of seawater will affect its chemistry and possibly reduce the detrimental effect upon the biology;

b) Techniques and avenues to investigate the effects are similar for both types of spills situations. Within the intertidal reaches of the estuary and emergent zones of the stream communities, oil coverage is more noticeable as it coats the organisms. However, the entire community must be investigated to determine alternate degrees of effect from the spill;

c) Sampling the biotic populations must be quantitative and qualitative in nature. Sampling the aquatic environment to quantify contaminant background, the entrapment, and the incorporation into the biomass of the community is essential to correlate the biological response with contaminant levels. In tracing these trace levels of spilled hydrocarbons, significant problems and short-comings with the available analytical procedures have been revealed. The ability to analyze low levels of hazardous materials free in the environment may prove to be an even greater analytical problem due to the diverse chemical nature of hazardous materials as a group.

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THE HAZARDOUS MATERIAL SPILL EXPERIENCE IN SHAWNEE LAKE, OHIO — A CASE HISTORY

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On June 2, 1971, approximately one and one half pounds of endrin solution mixed with strychnine treated corn in a one gallon plastic container was thrown into Pond Lick Reservoir which is referred to locally as Shawnee Lake. This lake is located in the Shawnee State Forest approximately ten miles southwest of Portsmouth, Ohio, and was a very popular recreational area with boating and fishing permitted. This lake is only about 1,000 feet long and approximately 250 feet wide at its widest point. Its greatest depth is 35 feet and averages about 15 feet. Fortunately this depth enabled a definite thermocline or stratification of the water to occur, separating the lake into two definite layers.

Needless to say, the results of throwing these two toxic substances into this small lake were immediate. The entire fish population was destroyed. The only surviving aquatic vertibrates were tadpoles which appeared to be unaffected by these pesticides.

Our Department took immediate action. We posted the area with warning signs. Our chief concern at this point was to contain these poisons within the lake in order to protect Pond Lick Creek and Turkey Creek which flows for only six and one half miles south to its confluences with the Ohio River. Cincinnati, only 100 miles downstream on the Ohio River, had been notified and was vitally concerned about protecting its water supply. Radio, television and newspapers cooperated in warning the public of this hazard. All water supplies were checked and the area surveyed to make certain that no livestock would be affected. All access roads were closed.

The crucial first step of isolating this reservoir was accomplished by our engineers and field staff in the Divisions of Forestry and Wildlife by sandbagging the spillway, building an earth-diversion dam upstream from the lake, and providing two 3,000 gallon per minute pumps and sufficient ten inch aluminum piping to enable Pond Lick Creek to bypass the now isolated reservoir. This bypass arrangement would take care of normal flows and 1.3 inches of rain per hour. In the event of a really heavy rain the limited capacity of the pumps would not be able to divert all this water. This made speed imperative. Bags of activated carbon were added to the spillway to remove any pesticide that might seep through. Any seepage was pumped back into the lake.

From the very beginning samples were taken and analysed from the plastic jug which was recovered from the water at various depths, from sediments and from aquatic animals. Endrin concentration in the lake was about nine parts per billion at this time. Strychnine was only detected in the container. None could be detected in the lake. Endrin is exceptionally stable. The product used was a wettable emulsion and as a result had mixed with all the surface waters in the lake. Endrin is extremely poisonous to fish even at concentrations as low as 0.2 parts per billion. It has a half life of from seven to twelve years, and, because of its potential for biological magnification through the food chain, can build up to concentrations of 100 to 10,000 times the initial concentration in water. This meant that we somehow had to completely remove all endrin to recognized safe limits. We also recognized that the necessary laboratory facilities and technical personnel had to be on site to run the various tests. We contracted with Ohio State University for use of its Gas-Chromatographs and provided temporary laboratory space and personnel to make the necessary chemical, biological and bio-assay tests on a continuous basis. Using fish as test animals on the discharge water was an additional safety precaution, even though our analytical instruments were much more sensitive. Our data indicated that most of the endrin was concentrated in the upper water levels.

We now had to decide on a method or methods for removal of the endrin and a clean up of the lake. We called upon people within our own State for advice and assistance. We called upon Federal agencies, local agencies and private consultants and industries that might assist. We had the best of cooperation from the local Sheriff and County Game Protector who reported the incident and apprehended the person who threw the poison jug into Pond Lick Reservoir. We also had the best of cooperation from the various representatives of the Federal Environmental Protection Agency who supplied technical work teams.

Some of the ideas suggested for resolving this problem were as follows:

1. Dilution
2. Spray irrigation
3. Adsorption—bentonite, fly ash
4. Biological removal
   a. sewage
   b. fish
5. Chemical
   a. cracking
   b. oxidation with ozone
6. Adsorption and filtration through activated carbon.
7. Physical removal by use of tank trucks.
8. Filter through alfalfa hay.

Most of the ideas were discarded as impractical or ineffective.

We first attempted to reduce the concentration of endrin in the reservoir by broadcasting approximately 7,000 pounds of 40 mesh granular activated charcoal which proved to be ineffective due to the fact that there was insufficient contact time before setting out. A cylindrical pilot plant was then made of one and one half foot diameter pipe, eight feet high and prepared by filling it with activated carbon and running the water into the bottom and out the top of this column. It proved to be very effective in removing the endrin. The lake water by this time had a concentration level of approximately seven parts per billion which was reduced to near zero by passing it through this eight foot column of activated charcoal. Based on this success, a large treatment plant was designed. The channel filter using an upflow system was essentially a 4 x 8 x 18 foot wooden box through which water was pumped in the bottom through coarse gravel covered with a mesh screen over which a six foot deep bed of charcoal was placed. This, in turn, was covered with a stainless steel screen to hold the charcoal in place. Although effective, the rate of filtering was quite slow, only about 80 gallons per minute. The filter had a tendency to clog and had to be backwashed several times during operation. To further complicate matters, we discovered that underground springs were feeding the lake at a faster rate than we could filter it. After filtering about two million gallons, it was decided that additional filters would be needed. A flume filter containing charcoal was then designed and constructed in the spillway outlet of the lake. The discharge from these filters were directed into a stilling flume below the lake where filtered water was retained until analysis indicated the endrin concentration was below a safe limit set at 0.1 parts per billion; well below the 1.0 part per billion established as a safe limit for human consumption.

Sediment samples in the lake indicated that the endrin was being adsorbed onto the organics in the lake sediments, and, since the lake level was not decreasing as rapidly as was hoped, we decided to attempt additional filtering with another, less expensive media such as humus, peat or straw. Baled hay containing some alfalfa and wheat straw was available locally so we tried that on a pilot plant basis. This proved to be very effective. A large filtering device was then constructed of wood to hold 166 bales of hay through which the water was filtered at a rate of approximately 1,500 gallons per minute. Since the bottom layer of water contained a lessor amount of endrin, we pumped the water from the bottom of the lake enabling us to lower the lake at a faster rate. Eventually the endrin in the descending waters reached a level of three to five parts per billion. The discharge from our hay filter worked like a charm. No detectable endrin could be found from the discharge. The lake was finally drained. Analysis of sediment along the banks was high in endrin—around 100 parts per billion. The bottom of the lake which contained very little organics was low in endrin.

The bottom and sides of the lake were cleaned and scraped and removed to an offsite area outside the immediate watershed for disposal. The area had previously been prepared by building low clay retaining walls into which the sediments from the bottom of the lake were disposed and sandwiched in between thick layers of impervious clay. There were about 6,500 cubic yards of this sediment which was distributed over an area of approximately two acres to a depth of eighteen inches. These contaminated sediments were further mixed with the clay that was eventually removed from the diversion dam. Analysis of these mixed sediments showed a concentration of less than 1.0 parts per billion which is considered less than the normal application rates recommended for agricultural pest control.

After almost three months the lake was fertilized, the banks reseeded and fish spawning devices were installed.

On September 1, 1971 the refilled lake was restocked with fish.

Three months later and a hundred thousand dollars shorter we completed what first appeared to be a hopeless task.

We have learned quite a bit from this experience and can take great pride in the response of the many agencies and individuals who helped in this effort.

If our Department were a military organization I would have sent special letters of commendation and an appropriate plaque to each individual who took part in the mobilization to clean up Pond Lick Reservoir. Since we are not, I have had prepared sample bottles of pure Pond Lick water, appropriately labeled and sent as a special memento to those who helped.

SPILL DAMAGE RESTORATION

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Section 12(f)(2)(A) of the 1970 Federal Water Pollution Control Act (P.L. 91-224) defines the removal of spilled hazardous polluting substances to include ". . . the taking of such action as may be necessary to minimize or mitigate damage to the public health or welfare, including, but not limited to, fish, shellfish, wildlife, and public and private property, shorelines and beaches."

The purpose of this paper is to explore the need for mitigating environmental damages and some possible means of implementing an effective program.

Prevention of spills is the first line of defense against environmental damage, and the development of effective prevention plans and a code of clean practice can effectively reduce spill incidents, but the unforeseen and sometimes unpreventable spills will continue to pollute our waters.

Rapid response resulting in containment and physical cleanup or neutralization of toxicity are, of course, the primary means to minimize the areal extent and severity of environmental damages when these spills occur. The containment of a soluble hazardous material spill in open waters is, at present, practically impossible. In these cases, most often the only practical response action is a warning to downstream water users. Environmental damages are usually inflicted until dilution decreases the level of pollutant below the toxic or damaging concentration. The resulting environmental damages range from subtle alterations of population balances by the elimination of sensitive or marginal species to obvious and massive fish kills. An example of the severity of environmental damage that can result is the recent phosphate mining waste discharge on the Peace River that was reported as severely depressing approximately seventy-five river miles of aquatic life.[1]

The time required for natural recovery from spill insults is extremely variable. Factors influencing this time include the general health of the upstream environment, flow rate of the waterway or flushing rate of impoundments and estuaries, persistence of the material, and the seasonal time of the spill. In a controlled experiment, Cairns showed that the benthic community of a fast-flowing mountain stream required a time period of about one month to recover from a sulfuric acid induced pH stress.[2] The "spill" conditions of the experiment can be described as mild, when compared to more toxic chemicals, such as insecticides, and of relatively short duration. The conditions for recovery in this situation were nearly ideal with a nonstressed upstream environment, rapid flushing, no damage to habitat or littoral life forms, and a less than total kill.

In 1967, a dike failure released approximately 130 million gallons of caustic solution from a fly ash holding pond into the Clinch River. As a result, some 200,000 fish were killed in a total of ninety river miles in both Virginia and Tennessee. Follow-up studies of benthic and fish communities indicated that full biological recovery was not achieved after two years.[3]

Blumer[4,5] has documented the long-term effects of oil spills on shellfish and estimated the recovery of shellfish populations from a diesel oil fuel spill in Buzzards Bay, Massachusetts, to be at least two years. Additionally, wide-range and long-term biological damages, resulting from oil spills in the marine environment, have been indicated from recent EPA investigations of spills in the Gulf of Mexico and Puget Sound.[6,7]

Preliminary data now exist which indicate a possible correlation between oil contaminated substrates and gonadal tumors in clams.[8] As more de-

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tailed studies become available, previously unknown long-term effects will probably be brought to light. The need for an accelerated restoration program to ease the long-term impact of spills is becoming increasingly important. In the case of persistent, slowly degraded materials (such as oil or chlorinated hydrocarbons), thorough and effective cleanup must be an integral part of aquatic restoration.

Lakes, impoundments, and estuaries have slow exchange or flushing rates when compared to free-flowing rivers and streams. A spill in such contained waters, may therefore, result in a longer exposure time for aquatic organisms and the probability of a higher percentage of mortality. As a higher percentage of any aquatic community is destroyed, the time required to establish pre-spill population densities is increased. The slow exchange rate also leads to significantly decreased benthic organism drift. In contained waters, slow drift repopulation will probably be the limiting factor in the recovery of the benthic community, and one would expect an overall decrease in productivity for at least one seasonal cycle.

Since most of our waterways are continually subjected to man-induced stresses such as continuous industrial and municipal discharges, agricultural chemical runoff, mine drainage, and silt loadings from construction, natural restoration may be significantly delayed and require many years to reach pre-spill quality. During the natural recovery processes, a succession of population balances can occur and exhibit varying degrees of stability. Because of a complex phenomena that may most easily be addressed as competition, certain species become predominant, and undesirable floral and faunal species may become established.

The minimization or mitigation of biological damages and the resultant denial of a beneficial water use such as recreational or decreased esthetic value can only take the form of accelerated restoration. A successful restoration program could significantly lessen the long-term impact of hazardous materials spills by returning a water body to its pre-spill condition in the shortest possible time. For example, the restoration of sport fishing within months rather than years would significantly minimize damages to the public welfare.

The impact of a major spill on aquatic life could be significantly lessened by the timely enlargement of the potential breeding stock. Organisms from experimental aquaculture facilities at universities and State hatcheries as well as selective harvesting from unaffected areas are potential sources of new breeding stock. Selective harvesting would distribute the impact of the spill over a larger area so that the local severity would be lessened.

There is, however, the potential for creating even larger scale ecosystem imbalances if due care is not exercised with the harvesting method. The use of cultured breeding stock does not carry this potential for harm, and would seem to be the method of choice when cultured organisms are available. A notable example of culture technology is that of shrimp. Postlarval shrimp are currently available on a limited scale at about 0.25 cents each. Future considerations should, therefore, be given to enlarging both the numbers and species of reserve organisms. Emphasis should be given to those species which are both commercially and recreationally valuable as well as to those organisms that occupy important niches in the food web.

Most States, today, levy a charge for fish killed in a pollution incident and efforts toward restoring the fish population are made. Restocking of game fish has sometimes improved sport fishing, but the effective period may be relatively short. For example, placing fish in a river or impoundment without restoring the necessary food sources, habitat, or water quality has little long-term beneficial effect. If possible, the fish will undoubtedly migrate to areas of the stream most agreeable to them. In impoundments where migration to suitable areas is not always possible, inadequate food supplies and spawning habitat will be manifested in depressed populations. Increasing knowledge of the delicate ecosystem balances and the interdependence of the many varied species within the aquatic environment indicates that a broader approach to restoring damaged waterways is needed.

To be effective, aquatic restoration must consider the physical habitat, food web organisms, fish, shellfish, vegetation, and other aquatic life as well as littoral life forms. The Environmental Protection Agency, through programs such as the Division of Oil and Hazardous Materials, is in the process of developing a comprehensive restoration and mitigation program concerned with the orderly rebuilding of all trophic levels within the aquatic ecosystem. The eventual goal of this or any restoration-mitigation effort should be the maximum diversity of all aquatic communities yielding a more stable ecosystem.

New techniques and knowledge must be developed in this area before a large scale program is functional. Typically, the tools required for such a program may be summarized as: (1) baseline data, (2) characterization of typical ecosystems and the food web interrelationships, (3) long-term chronic effects of spills, (4) aquatic population dynamics and the factors that influence them, (5) effects of physical alterations of habitat on ecosystems, and (6) effects of natural stresses.

Baseline data are critical for the accurate assessment of spill damages and for providing a target for restoration activities. Because of the great variety of ecosystems, as well as the effect of local and seasonal conditions, baseline information should be gathered from an unaffected area near the spill and at a corresponding season.

This highly specific data should be backed up by a more general characterization of typical ecosystems. A great deal of information is currently available and this task could quite conceivably be accomplished through a literature review and compilation of existing data. The generated profiles should highlight the predicted species and food web interrelations that one would expect to find in each typical ecosystem. Such data would be valuable in assessing the impact of previous man-induced or natural stresses on the aquatic environment.

Research aimed at established chronic effects of hazardous materials on aquatic organisms must be expanded. For example, a sub-lethal effect may, in the next spawning season, be expressed at impaired reproductive capability. Mutagenic and teratogenic effects may not be observed for at least one generation. The eventual impact of these potential sublethal effects can be as severe as immediate mortality. The success of a restoration effort may, in some cases, hinge on the degree of accuracy with which chronic effects are assessed.

Attempts to repopulate a waterway by species introduction will require a firm understanding of population dynamics and the factors that influence them. A familiar form of population dynamics management is that of using large predator fish to control the population of smaller, more prolific species. This concept of predator pressure needs to be expanded and applied to all communities within the ecosystem.

In addition to chemical and biological factors, consideration must be given to the effects of physical alterations of the habitat. Cleanup operations to remove dense, insoluble materials such as creosote wastes from the water may necessitate dredging of a stream or lake bed. Since the detrimental effects of stream channelization and dredging on aquatic life have been documented,[9, 10, 11] a restoration effort must evaluate these effects.

Finally, natural stresses and normal seasonal fluctuations in community balances must be evaluated in terms of their effect on damages and restoration. These factors will also be important considerations in assessing the liability for environmental damages.

One approach to a viable restoration effort could be through the use of response teams assembled in key areas. Following a spill, such a team could be activated and attempt a variety of techniques in real situations and environments, with follow-up studies gauging the degree of success. Circulation of a newsletter to all participating teams describing all attempts both successful and nonsuccessful would decrease duplication of effort and eventually evolve supportive data and proven techniques.

Through the Federal Excise Tax on firearms and fishing tackle, Americans paid forty million dollars to expand, develop and preserve our wildlife resources. An effort should be made to protect this investment by the implementation of a restoration program that effectively reverses spill damages.

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